THE REGIONAL TREATMENT OF TEXTILE AND INDUSTRIAL EFFLUENTS

Report to the
WATER RESEARCH COMMISSION

by

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Executive Summary

1 Background

Effluent from the textile finishing industry is generally highly coloured and of a complex and variable nature. Conventional biological waste water treatment works are not designed to treat this type of effluent with the result that colour and chemicals are not sufficiently removed and enter the receiving water bodies. This gives rise to public complaints, either due to aesthetic reasons or because it precludes some down-stream use of the water.

The South African textile industry is the sixth largest employer in the manufacturing sector, with 80 000 people employed directly, an additional 200 000 indirectly in dependent industries and supports 80 000 cotton workers. It has local annual sales of R 7,7-billion and is the eleventh largest exported of manufactured goods. In addition, it is the second largest user of electricity from Eskom and the second largest rate payer of rates and taxes in towns and cities across South Africa.

The South African textile industry has been in a state of decline over the last 13 years and with the lowering of textile tariff rates, the industry is going to become increasingly exposed to international competition over the coming years. Therefore, in order for the textile industry to survive it must become more export orientated and economically competitive. However, with the introduction of ecolabelling, it will become increasingly difficult to export to the European Union and the United States of America unless textiles are manufactured according to this environmental legislation.

This project has focused on the Pinetown and Hammarsdale regions due to the number of textile mills in these areas discharging to the local wastewater treatment works. In both areas, the final effluent from the treatment works were not complying with the standards set by the Department of Water Affairs and Forestry (DWAF), especially with regard to colour. Previous research projects involving the textile industry had focused on the in-house recycling of water and chemicals, with the concentrates being discharged to sewer. Due to the increasing environmental pressure, both locally and world-wide, the South African textile industries must work towards reducing their environmental impacts by improving their processes and choice of chemicals and by addressing the problem of treating the concentrates.

This project was initially to have been undertaken by Umgeni Water, but was taken over by the Pollution Research Group.

2 Project Aims

The main aims of the project were to :

- determine the fate of textile and specific industrial effluents through treatment processes;

- determine the effect of specific textile and industrial effluents on sewage treatment processes and on the quality of the final effluent;
- investigate the addition of polymers, flocculants or adsorbents at a sewage works to improve the removal of specific classes of pollutants;
- investigate the addition of processes within a sewage works to improve the removal of specific pollutants;
- investigate the treatment of specific concentrates which could be segregated at source;
- investigate the use of anaerobic digestion for the treatment of dye concentrates;
- initiate an effluent monitoring and targeting programme at selected sites in order to minimise waste, reduce effluent load, predict the nature of the effluent and to target problematic streams.

This project was therefore initiated to investigate ways of treating textile effluents, either on-site or at the waste water treatment works, with the focus being on colour removal. In addition, waste minimisation and point source reduction techniques were to be introduced into the factories to reduce water, chemical and energy consumptions, thereby reducing the volume of effluent produced and making savings for the industry. At the same time, the importance of improving their environmental performance, such as replacing or eliminating chemicals classified as being harmful to the environment, was stressed.

3 Project Approach

Treatment options for the removal of colour can be broadly divided into three categories; chemical, biological and physical. Chemical treatment involves the addition of chemicals to the effluent which cause decolourisation through either oxidative or reductive mechanisms. Options for biological treatment may be single phase aerobic or anaerobic processes, or a combination of the two. Physical treatment involves the flocculation of the dye and its removal by flotation or sedimentation. Membrane technologies such as nanofiltration are also used. Table 1 gives a summary of the various available effluent treatment technologies. The advantage of anaerobic biological processes over the other systems is that they are more economical in day to day running costs and are essentially self-sufficient. From a survey of the literature, it was concluded that aerobic treatment systems do not sufficiently remove colour from textile effluents, whereas anaerobic digestion showed the potential for non-specific colour removal. Therefore, the feasibility of using anaerobic digestion as a possible treatment route for textile effluents was investigated.

Reactive dyes have been identified as being the most problematic dye class with respect to treatment as they are water soluble and have relatively low exhaustion rates and are therefore present in high concentrations in the effluent. Due to their solubility they are not readily adsorbed onto floc or to biomass and hence do not report to the anaerobic treatment section at a waste water treatment works. For this reason, initial laboratory studies focused on the decolourisation of a single azo reactive dye, C.I. Reactive Red 141 (Fig 1). This dye was chosen because (i) it is a reactive dye, (ii) it is an azo dye, the basis of which makes up approximately 80 % of the dyes used today in the textile industry, and (iii) red is highly visible to the naked eye.

Table 1 : Summary of available textile effluent treatment technologies

Technology	Examples	Advantages	Disadvantages
Coagulation/ flocculation	alum lime iron polyelectrolytes	* simple equipment * relatively rapid colour removal * significant reduction in COD	* large volumes of sludge may be generated * continual addition of chemicals * high running costs * carry-over of polyelectrolytes may affect sewage works
Membranes	reverse osmosis nanofiltration ultrafiltration	* removes impurities of particular molecular masses * good colour removal * fast * can handle large volumes	* high capital costs * some effluent cannot be treated * concentrate contains almost all impurities * concentrate must be treated by another technology prior to disposal * impurities in purified stream may be too high for re-use * regular cleaning is required
	dialysis	* purified stream could be re-used * cation stream could be re-used to regenerate water softener, or as caustic or carbonate in the dyeing process	* portion of the effluent is not treated * concentrate contains almost all impurities * at least one of the concentrates must be treated by another technology * organic material could foul membranes * non-ionic species are not removed * capital and operating costs not known
Adsorbents	activated carbon, silica, charcoal, peat, synthetic polymers etc.	* good colour removal * simple technology * low operating costs for some adsorbents	* high capital cost * slow * can only handle small volumes * regeneration or disposal costs * no single adsorbent is suitable for all dye types * required dosage may be high
Oxidation	Ozone	* good colour removal * can handle large volumes	* High capital costs * high operating costs * not effective at removing colour from all dye types
	Fenton's reagent	* rapid decolourisation * simple operation * sludge enhances sewage works operation	* unknown oxidation products * high running costs
	UV / peroxide UV / catalyst	* good colour removal * powerful oxidant * effective at destroying organic compounds	* high capital costs
	chlorination	* inexpensive * good colour removal	* chlorinated by-products
Reduction	tin chloride hydrosulphite	* good colour removal * effective for decolourising azo dyes	* aromatic amines may be formed * incomplete degradation
Biological	Aerobic	* suitable for removing colour due to insoluble dyes * usually results in mineralisation of dyes	* does not remove colour due to soluble dyes such as reactives * large volumes of sludge are generated * large energy requirements
	Anaerobic	* non-specific colour removal * decolourises most dyes through reduction mechanism * methane produced can be used as energy on-site	* unknown degradation products * high capital cost
Evaporation		* concnetrates effluent stream	* does not "treat" colour
Irrigation		* inexpensive	* detrimental effect on soil * suitable only for uncoloured and non-toxic streams

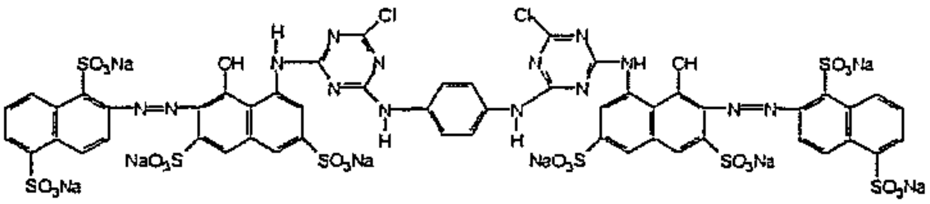

Fig 1: Structure of C.I. Reactive Red 141.

This laboratory study was then extended to include a range of reactive dyes and finally, full-scale trials were carried out at the Umbilo Sewage Purification Works (USPW) in Pinetown. Similar full-scale trials are underway in Hammarsdale and are due to be completed at the end of 1996. The details of this work will be added as an addendum to this final report.

In conjunction with the anaerobic study, the use of chemical reducing agents to decolourise azo dyes was investigated in the laboratory. Initial studies also concentrated on C.I. Reactive Red 141, but were extended to include other azo dyes. Analytical techniques such as thin layer chromatography (TLC), column chromatography, nuclear magnetic resonance spectroscopy (NMR) and high performance liquid chromatography (HPLC) were used to purify the dyes, confirm their structures and separate and identify the degradation products of the dyes. Some investigations into the use of electrochemistry to decolourise azo dyes are also underway. In addition, a project has been initiated at the Umbilo Sewage Purification Works in Pinetwon to identify the degradation products formed during decolourisation of textile dyes and effluents by the Fenton's reagent. ML Sultan Technikon will also be involved in this investigation.

As mentioned earlier, in addition to investigating methods of removing the colour from textile effluents, waste minimisation surveys were conducted within the textile factories to promote good house keeping and process optimisation. This results in savings in water, chemicals and energy and reduces the effluent volume and load from the industries.

4 Summary of Results

4.1 ANAEROBIC DECOLOURISATION

An in-depth laboratory investigation was carried out into the decolourisation of C.I. Reactive Red 141 under anaerobic conditions. The rate of declourisation and the factors affecting decolourisation were determined. These included:

- the effect of prior exposure of the biomass to the dye;
- the initial dye concentration;
- additional carbon source requirements;

- the presence of additional electron acceptors;
- the redox potential of the system and
- adsorption to the biomass

It was found that while prior exposure of the biomass to the dye did not increase the rate of decolourisation, it did render the micro-organisms resistant to previously inhibitory concentrations of the dye. It is known that decolourisation of azo dyes occurs through reduction of the azo bond with subsequent destruction of the chromophore. The rate of decolourisation was first order with respect to dye concentration, although this was found to decrease with increasing initial dye concentrations. This was attributed to the accumulation of potentially toxic metabolites in the system. An additional carbon source (e.g. glucose) was found to be necessary to maintain the microbial metabolic state as was observed by the reduced rate of decolourisation in the absence of the glucose. The presence of nitrate in the system resulted in inhibition of decolourisation whereas sulphate had no effect on the decolourisation rate. This led to the conclusion that the redox potential of the system was important, with C.I. Reactive Red having a potential of between that of nitrate and sulphate. Continuous redox potential measurements confirmed that decolourisation only occurred once all the nitrate in the system had been reduced and that a potential of less than -450 mV (SCE) was conducive to rapid decolourisation. Adsorption of the dye to the biomass did play a role in the initial stages of decolourisation, but it was found that the adsorbed dye was subsequently decolourised and therefore no distinction was made between abiotic and biological decolourisation. The degradation products of the dye after anaerobic digestion were isolated and identified and found to be consistent with reduction of the azo bond. These metabolites were not degraded further under anaerobic conditions.

As mentioned, anaerobic decolourisation of C.I. Reactive Red 141 requires the presence of supplemental labile carbon to maintain the anaerobic microbial population in an active state. Laboratory studies used glucose as a carbon source, however this would not be feasible on a large industrial scale. Therefore, the enrichment of biomass which was capable of degrading the organic content of a cotton scouring effluent was investigated. It was found that this microbial population was able to decolourise C.I. Reactive Red 141 while digesting the scour effluent organics, giving rise to a final effluent with reduced COD, pH and colour. Decolourisation was found to be first-order with respect to dye concentration, and to be inhibited by the presence of nitrate in the feed. This research shows the possibility of combining energy-rich and highly coloured textile effluents in an anaerobic digester with the aim of reducing the effluent COD, pH and colour.

The anaerobic decolourisation of 18 reactive dyes was investigated. Of these 14 were azo dyes, 3 phthalocyanine dyes and one was based on the anthraquinone chromophore. All but one of the azo dyes tested were decolourised by 70 to 90 %. The phthalocyanine dyes tested gave a wide spread of results with decolourisation efficiencies ranging from 25 to 90 % and the anthraquinone dye showed little decolourisation. These results are consistent with those reported in literature.

In order to determine the fate of dyes in a conventional waste water treatment works, a trial was conducted at Umgeni Water's Hammarsdale Waste Water Treatment Works during the shut-down period of the textile industries where C.I. Reactive Red 141 was dosed into the works prior to the anaerobic zone in one of the Bardenpho reactors. It must be noted that due to the textile factory shut-down, the flow into the works was lower than usual and therefore the residence times in the various zones was increased leading to more anaerobic conditions than were normally experienced. No colour could be detected after 30 min and laboratory tests using the sludge from the anaerobic and anoxic zones confirmed that decolourisation was occurring through reduction of the azo bond. Based on the success of this experiment, full-scale trials were initiated at the Umbilo Sewage Purification Works (USPW) in Pinetown.

The USPW allowed the PRG the use of one of their four heated primary digesters for this investigation. The trial began at the end of May 1994 and continued for 5 months. Concentrated reactive dyebath effluent was obtained from Ninian and Lester in Pinetown. The effluent was trucked to the treatment works on a daily basis (Monday to Friday) and discharged into the empty sump at the primary sludge pump station. The digester chosen for the trial (digester 2) was isolated from the other digesters and the dye effluent pumped to this digester. Digester 3, which received no dye effluent was used as the control. On average, 3 kl/d was trucked to USPW. A laboratory-scale digester was run in conjunction with the full-scale trial in order to simulate the conditions in the primary digester except that it was dosed at approximately 1.5 times the dye load of the full-scale digester.

A visual comparison of the supernatant of digester 2 and the laboratory digester and that of digester 3, showed no difference in colour and it was concluded that decolourisation of the dye effluent was occurring. However, high levels of sodium and sulphide concentrations were recorded in both the full-scale and laboratory digesters. This was attributed to the sodium sulphate used in the reactive dyeing process. While the levels in the experimental digester never reached a point where digester stability was threatened, the sulphide levels in the laboratory digester increased rapidly until they reached a concentration of 400 mg/l, at which point digester failure was noted. However, it must be remembered that this digester was shock-loaded and was not allowed time to acclimate to the dye effluent. It is suggested that if anaerobic systems are to be used as a treatment route for textile effluents, substitutions for sodium sulphate in the dyeing process, such as sodium chloride or sodium carbonate, should be investigated.

The feasibility of conducting similar full-scale trials at the HWWTW is now being investigated. Initial laboratory tests have indicated that the redox potential of the sludge in the anaerobic and anoxic zones could be sufficiently low to enable decolourisation of azo dyes. A detailed redox potential profile of these zones is currently being recorded. Serum bottle test will also be conducted using the sludge from these zones to investigate the decolourisation of other classes of dyes under anaerobic conditions.

4.2 CHEMICAL DECOLOURISATION

As with the anaerobic study, all investigations were initially carried out on C.I Reactive Red 141, but were later extended to 3 other dyes; benzeneazo-2-napthol; *p*-sulphpbenzeneazo-2-napthol and C.I. Reactive

Red 2. All experiments involved determining the structure of the dye by a number of analytical techniques, reducing the dye chemically and identifying the degradation products.

The commercially available formulations of C.I. Reactive Red 141 and C.I. Reactive Red 2 were found to be impure and methods of purifying the dye were investigated. HPLC was found to be the most suitable technique. Stannous chloride was found to be the most effective chemical reducing agent. Solutions of the dyes were prepared in methanol and were refluxed with stannous chloride in hydrochloric acid until decolourised. On cooling, precipitates were formed which were separated and analysed by proton NMR. The remaining solutions were separated by TLC. By identifying the degradation products, it was evident that in all four azo dyes investigated were decolourised through cleavage of the azo bond.

To confirm that decolourisation under anaerobic conditions was occurring through reduction of the azo bond, the dyes were subjected to anaerobic digestion and then analysed for degradation products. Similar degradation products were identified as from chemical reduction, thereby confirming the mechanism of decolourisation.

As mentioned earlier, this project focused on both the Pinetown and Hammarsdale regions. During 1990, numerous public complaints were received by the Department of Water Affairs and Forestry (DWAF) regarding the presence of colour in the Umbilo River in Pinetown. The cause of the colour was traced back to the discharge point of the Umbilo Sewage Purification Works (USPW). Pressure was placed on the USPW to reduce the colour in the final effluent and this resulted in increasing pressure on the Pinetown textile industries to reduce the colour load in their effluents. This resulted in the formation of the Pinetown Colour Committee in May 1990, which consisted of representatives from the USPW, DWAF, the textile industries, the Water Research Commission (WRC) and the University of Natal. Explochem Water Treatment was commissioned to investigate methods of removing the colour either at the factory fence or at the USPW. The committee met for four years, during which time it was decided that no colour limit would be set for the discharge from USPW, but that it must not give rise to public complaints, and a limit of 400 ADMI was set for the textile industries.

Two methods were investigated in detail, namely Fenton's Reagent (Fenex process) and COLFLOC, a cationic polyelectrolyte. The Fenex process was found to be the most effective, both in terms of colour removal and costs. As a result of this study, Fenex plants have been commissioned at 3 textile factories in Pinetown.

4.3 WASTE MINIMISATION

Waste minimisation is a technique which involves a study of the processes in use at an industry and the identification of areas within the manufacturing processes were savings can be made in terms of water, energy and chemical consumption. This leads to a reduction in both the volume of effluent from the industries as well as the effluent load entering the wastewater treatment works.

At the outset of this project, it was envisaged that waste minimisation surveys would be conducted at all the textile mills in the Hammarsdale area. This region was chosen due to the large number of textile industries in close proximity to one another. However, with the shift of focus onto the Pinetown region, this work was put on hold until 1995. To date, waste minimisation surveys have been conducted at de Nim (Hammarsdale; 1993), David Whitehead and Sons (Tongaat; 1994 and 1995), Gelvenor (Hammarsdale; 1995) and Natal Threads (Hammarsdale; 1995). The last two were conducted as part of a joint project with the Environmental Monitoring Group (EMG) in Cape Town and is funded by a Dutch organisation , HIVOS (Humanistische Instituut voor Ontwikkelingssamenwerking). The second survey at David Whitehead and Sons was conducted in conjunction with Ecoserv.

5 *Realisation of Objectives*

From the results obtained during the course of this project, it is evident that the objectives have been achieved. From a survey of the available literature, it was determined that textile dyes, and in particular reactive dyes, are not sufficiently removed or degraded in conventional aerobic biological treatment processes, and that any colour that is removed occurs through adsorption onto the sludge. Anaerobic digestion however showed the potential for non-specific colour removal and was therefore investigated in detail. The results of the laboratory and full-scale trials have indicated the feasibility of using this system to treat concentrated reactive dyebath effluent. The combination of decolourisation with the treatment of high COD streams to produce an effluent that has reduced colour, COD and pH showed promising results. It was found that high concentrations of textile dyes were inhibitory to the anaerobic micro-organisms, but that this could be overcome by acclimating the sludge to the effluent. In the case of azo dyes, the mechanism of decolourisation was found to occur through cleavage of the azo bond to form the corresponding aromatic amines. These metabolites were not degraded further under anaerobic conditions. The possible toxicity of these amines is of concern. Chemical analysis was used to identify and characterise the dyes and dye degradation products.

The use of polymers and flocculants was not investigated as these processes remove colour through adsorption mechanisms and when discharged to sewer, report to the solid phase and therefore to anaerobic digestion. They were therefore seen as a means of transporting the colour to the anaerobic system and were not studied further.

Waste minimisation surveys were conducted at some textile industries and reports submitted detailing where savings could be made in terms of water, chemicals and energy. This section of the project is still under investigation.

6 *Recommendations*

- Reactive dye concentrates can be treated in a conventional anaerobic digester;
- The combination of an anaerobic-aerobic treatment system should be investigated;

- Further research into the co-treatment of dye concentrates and the high COD streams such as scouring and desizing effluents should be conducted;
- The toxicity of dye degradation products need to be determined;
- A waste minimisation guide should be prepared for the textile industry;
- Factories should investigate implementing waste minimisation, effluent recycling and pollution prevention .

Further research is being conducted at the Hammarsdale Waste Water Treatment Works into the feasibility of using a dedicated Bardenpho reactor to treat dye concentrates. Waste minimisation surveys are currently being conducted at textile industries in the Hammarsdale area as part of a joint project with the EMG. Both these project are due to be completed at the end of 1996. The reports will be available from the WRC in 1997.

7 *Technology Transfer*

- The residence time distribution test carried out on the digester used in the full-scale trials at USPW was interpreted using IMPULSE, which was developed during the course of WRC project no. 363 entitled *The Development and Evaluation of Small-scale Potable Water Treatment Equipment.*
- During the course of the project, ad-hoc assistance has been given to:
  - Pinetown Colour Committee
  - Durban Municipality
  - Pinetown Municipality
  - Ninian and Lester
  - David Whitehead and Sons
  - Explochem
  - ECOSERV
  - Department of Water Affairs and Forestry
- The PRG has also been approached by the Lesotho National Development Corporation (through the kwaZulu-Natal Department of Water Affairs and Forestry) to assist them in developing a strategy for treating textile effluents. The request was motivated by official approaches by the South African Government to the Lesotho Government about the deteriorating water quality in the Caledon River and its effect on the South African users.
- Joint projects are underway with the following persons or organisations:
  - Umgeni Water (who are funding Mr C Bell for his MScEng)
  - Umbilo Sewage Purification Works
  - ML Sultan Technikon
  - Ms Cynthia Carliell (Loughborough University, United Kingdom)
  - Prof. Alberto Rozzi (Italy)
  - Environmental Monitoring Group
  - Mr Raymond Auerbach (Farmers Support Group, University of Natal, Pietermaritzburg)

- 1 MScEng and 1 MSc have been awarded and there are two current MScEng studies.
- 4 paper and 5 poster presentations have been made at various conferences, 2 papers have been published in Water SA and 2 further papers have been accepted for publication in Water SA.

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- Natal Threads Pty (Ltd)
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- ICI
- Umgeni Water
- Department of Water Affairs and Forestry

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Abbreviations

AA	Atomic absorption
ADMI	American Dye Manufacturers Institute
BOD	Biological Oxygen Demand
CC	Column chromatography
C.I.	Colour Index
CFC	Chloro-flouro carbons
COD	Chemical Oxygen Demand
DWAF	Department of Water Affairs and Forestry
EMG	Environmental Monitoring Group, Cape Town
EPA	Environmental Protection Agency, United States of America
ETAD	Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers
EU	European Union
GATT	General Agreement on Tariffs and Trade
HPCE	High performance capilliary electrophoresis
HPLC	High performance liquid chromatography
HWWTW	Hammarsdale Waste Water Treatment Works
IR	Infra-red
ISO	International Standards Organisation
ISP	Industrial Strategy Project
MRR	Maximum rate ratio
NMR	Nuclear magnetic resonance spectroscopy
PCP	Pentachlorophenol
PRG	Pollution Research Group
RTD	Residence time distribution
SABS	South African Bureau of Standards
SCE	Saturated calomel electrode
TLC	Thin layer chromatography

TOC	Total organic carbon
UK	United Kingdom
UND	University of Natal, Durban
USPW	Umbilo Sewage Purification Works
UV	Ultraviolet
WRC	Water Research Commission

Glossary

Acclimation	The adaptation of a microbial community to degrade a previously recalcitrant compound, through prior exposure to that compound.
Activated sludge	A mixed association of microorganisms which aerobically decompose waste in an aerated effluent treatment system.
Adaptation	A change in the microbial community that increases the rate of transformation of a test compound, as a result of prior exposure to that test compound.
Adsorption (dye)	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.
Aerobe	A microorganism capable of growing and metabolizing in the presence of free oxygen ie. in an aerobic environment.
Anaerobe	A microorganism capable of growing or metabolizing in the absence of free oxygen ie. an anaerobic or anoxic environment. These microorganisms may be facultative or obligative, the latter will perish in the presence of free oxygen.
Anoxic	An environment where oxygen is present in the form of compounds such as nitrate or sulphate.
Azo dyes	Dyes which contain at least one azo group (-N=N-), and can contain up to four azo groups.
Biodegradable	A property which allows the microbial decomposition of an organic compound to inorganic molecules such as carbon dioxide, methane and inorganic salts.
Dyeing auxillaries	Chemicals used in the dyeing process to aid the dyeing of the cloth / yarn.
Enrichment	Selection of microorganisms with certain characteristics, from a mixed culture, through manipulation of culture conditions.

Fenex Process	The use of Fenton's reagent to remove colour from textile effluents at pH 3.
Fenton's Reagent	Hydrogen peroxide and ferrous sulphate.
Metabolites	Intermediate compounds formed during dye dissimilation.
Mineralisation	Microbial decomposition of an organic compound to inorganic constituents such as carbon dioxide, methane and water.
Xenobiotic	A compound not found in nature, i.e. synthetic; or a compound found in nature, but in atypical concentrations.

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ANNEXURE 20	**S J Godefroy, C M Carliell, N Naidoo, B S Martincigh, D A Mulholland, C A Buckley and E senior**, *Regional Treatment of Textile Effluent*, Extended Abstract, Water Institute of Southern Africa, Durban, 24 to 27 May 1993.
ANNEXURE 21	**C M Carliell, S J Barclay, N Naidoo, C A Buckley and E Senior**, *Anaerobic Decolourisation of Azo Dyes,* Extended Abstract, 7th International Symposium on Anaerobic Digestion, Cape Town, 23 to 27 January 1994.
ANNEXURE 22	**D A Mulholland and N Naidoo**, *The Identification of Dyes and Dye Degradation Products*, Extended Abstract, South African Chemical Soceity, Frank Warren Conference, Avontura-Aldam, Free-State, 2-7 April 1995
ANNEXURE 23	**N Naidoo, D A Mulhollnd, S J Barclay and C A Buckley**, *The Identification, Separation and Degradation of an Azo Reactive Dye (C.I. Reactive Red 2)*, Abstract, Organic Heterocyclic Chemistry Conference , University of Hong Kong, 13-16 August, 1995.
ANNEXURE 24	**S J Barclay**, *The Pinetown Colour Committee : An Unique Solution to Solving the Problem of Colour in the Umbilo River.*
ANNEXURE 25	**SJ Barclay, CM Carliell and CA Buckley**, *Treatment of Exhaust Reactive Dyebath Effluent using Anaerobic Digestion*, Extended Abstract, WISA '96, Water Institute of Southern Africa conference, Port Elizabeth, 20-23 May 1996.

ANNEXURE 26	**CB Bell, SJ Barclay and CA Buckley,** *Decolourisation of Textile Effluent using a Modified Bardenpho Nutrient Removal System,* Extended Abstract, WISA '96, Water Institute of Southern Africa conference, Port Elizabeth, 20-23 May 1996
ANNEXURE 27	**CM Gilfillan, SJ Barclay, S Law and CA Buckley,** *An Assessment of the Environmental Performance of the Textile Industry in South Africa,* Extended Abstract, WISA '96, Water Institute of Southern Africa conference, Port Elizabeth, 20-23 May 1996

The above annexures are available from the Water Research Commission on request.

Chapter 1

Introduction

1.1 The South African Textile Industry

The South African textile industry is the sixth largest employer in the manufacturing sector, with 80 000 people employed directly, an additional 200 000 indirectly in dependent industries and supports 80 000 cotton workers. It has local annual sales of R 7.7-billion and is the eleventh largest exporter of manufactured goods. In addition, it is the second largest user of electricity from Eskom and the second largest payer of rates and taxes in towns and cities across South Africa (Anon).

Over the past 13 years, the South African textile industry has been in a state of decline and with the lowering of textile tariff rates, the industry is going to become increasingly exposed to international competition over the coming years (Maree, 1995). Therefore, in order for the textile industry to survive it must become more export orientated and economically competitive. However, with the introduction of ecolabelling, it is becoming increasingly difficult to export to the European Union and the United States unless textiles are manufactured according to this environmental legislation (see Chapter 3). The South African textile industries must therefore work towards reducing their environmental impact and increasing their efficiency by pollution prevention.

1.2 The Textile Processing Industry

A schematic outline of the main stages in the processing of natural fibres (wool and cotton) and synthetic fibres is given in Fig 1.1, with the processes producing liquid effluent marked with an E. This study concentrated on cotton and synthetic textiles. A summary of these processes is given below and a more detailed description in Annexure 1.

Sizing : This involves coating the yarn to protect it against the abrasive action in the weaving loom. Different sizes are used for different yarns. For example, starch is used for cotton and polyvinyl alcohol is used for polyester. The effluent from sizing is high in chemical oxygen demand (COD), but generally has a high biological to chemical oxygen demand ratio (BOD : COD).

Desizing : This involves the removal of sizes from the fabric prior to further processing. This effluent generally has a high organic load and is characterised by high COD values.

Scouring : Subsequent to desizing, any remaining natural impurities such as pectins and waxes are removed. This is done by washing the fabric with detergents under hot alkaline conditions. This effluent has high COD and pH values and a strong yellow-brown colour.

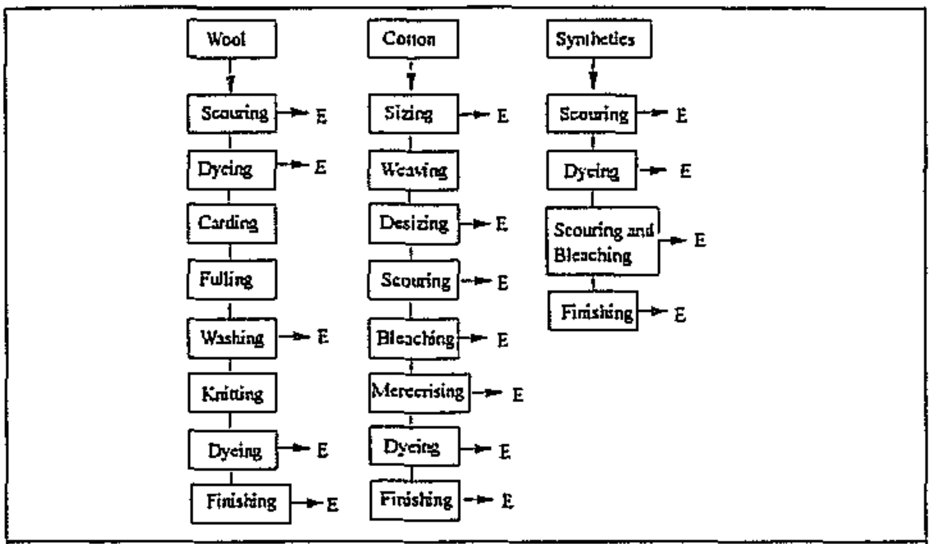


Fig 1.1: Simplified processing sequence for some textile fibres. E represents liquid effluents requiring treatment.

Bleaching : In this process, the whiteness of the fabric is improved by means of oxidising or reducing agents. Bleaching effluents do not usually contain high concentrations of organics. In most cases, hydrogen peroxide has replaced sodium hypochlorite as a bleaching agent.

Mercerising : Mercerising is the treatment of cellulosic fibres with a concentrated solution of sodium hydroxide to improve the water absorbency and therefore dye affinity, and also imparts a sheen to the fabric. The effluent is characterised by high pH values.

Dyeing : Different classes of dyes are used for different fabrics and each class requires a specific dyeing procedure. A classification of the various fabrics and dyes is given in Table 1.1. Dyeing can either be performed in discontinuous batch dye machines or in a continuous range. The volume of effluent produced from a batch process is far greater as between 4 and 10 rinses are required after dyeing to produce acceptable quality goods. The total volume of effluent produced depends on the liquor ratio (i.e. the volume of water used per kilogram of fabric). Liquor ratios range from 6 : 1 to 20 : 1, with 10 : 1 being a convenient average ((Buckley, 1992). The concentration of dye in the effluent is determined by the dye exhaustion properties and ranges from 95 to 98 % for acid, basic and disperse dyes, through 60 to 80 % for reactive dyes and 40 to 60 % for the balance of the dyes (Buckley, 1992). After discharging a batch dyebath, 90 % of the unfixed dye and auxiliary chemicals are present in the first drop (exhausted dyebath) giving rise to a low volume, concentrated, highly coloured effluent. Subsequent rinses become more dilute giving rise to large volumes of coloured effluent with a low organic load. Table 1.2 gives an example of how the concentration of dye in an effluent can be calculated (Pierce, 1994).

Table 1.1 : Fibre classification and associated dyes (Buckley, 1992)

	Fibre	Source	Name	Dyes used
Hydrophilic	cellulose	natural	cotton, linen, jute, paper	direct, sulphur, vat, azoic, reactive, metal complex
		regenerated	viscose, rayon	
	protein	natural	wool, mohair, angora, silk	acid, reactive, mordant, metal complex
Hydrophobic	polyamide	synthetic	nylon	acid, mordant, direct, disperse, reactive, metal complex
	polyester	synthetic	terylene	disperse, azoic, vat
	polyacrylonitrile	synthetic	acrylic, orlon, dacron	basic, disperse
	cellulose acetate	synthetic		disperse, azoic, vat
	cellulose triacetate	synthetic		disperse, azoic, vat

Printing : Printing involves the coating of the fabric with dye pastes in various colours and designs. Again, different dye classes are used for different fabrics. Some print pastes may contain solvents to improve the quality of the print. The printing process itself produces very little effluent, but large volumes of highly coloured effluent are produced during the washing of the fabric after printing and low volume, concentrated, highly coloured effluent is produced from the print kitchens.

Table 1.2 : Calculation of dye concentration in the effluent from Jet dyeing with reactive dyes

Fabric	100 % cotton
Batch size	250 kg
Dye class	Reactive
Depth of shade	2 %
Dye fixation	70 %
Liquor ratio	10 : 1
No. of baths	10.00
Weight of dye applied	5 kg (250 x 0.02) (batch size x depth of shade)
Weight of unfixed dye	1.5 kg (5 x 0.03) (mass of applied dye x % unfixed dye)
Total water usage	25 000 l (250 x 10 x 10) (batch size x liquor ratio x no. of baths)
Concentration in effluent	60 mg/l (1.5 / 25 000) (mass unfixed dye / total volume)

Finishing: This is the last process prior to final inspection and delivery. It involves both chemical and physical processing of the fabric. The fabric is coated with chemicals to improve its handle, fastness properties and its appearance, while physical methods such as sueding or brushing can alter its handle.

Effluent produced from finishing is of a low volume, but may contain toxic chemicals such as formaldehyde and solvents.

Waste water from the textile finishing industry is highly coloured and of a complex and variable nature. In general, the effluent streams have a high pH, are high in COD and BOD, are high in conductivity and contain auxiliaries such as detergents, bleaching agents, softeners and finishing chemicals. Of all these characteristics, colour has received the most attention and is a universal problem, both in terms of measurement and the setting of limits and in its removal from textile effluent streams.

1.3 The Problem of Colour

Colour in textile effluent arises from dyeing and printing processes, with the degree of colouration being dependent on the colour / shade dyed and the type of dye used. Water insoluble dyes, such as disperse or vat, have good exhaustion properties and the residual can be removed by physical methods such as flocculation or through adsorption. When textile effluent is discharged to a sewage works, colour due to these dyes is removed in the primary settling stages, with the water soluble dyes passing to biological treatment (conventionally aerobic processes). Of these dyes, reactive dyes are the most problematic as they are not easily adsorbed onto the biomass and, on average, 90% of reactive dyes entering a sewage works will pass through unchanged and be discharged to the river (Pierce, 1994).

Reactive dyes are coloured components capable of forming covalent bonds between the dye molecule and the fibre. The reactive system of these dyes react with ionised hydroxyl groups on the cellulose substrate by a nucleophilic substitution reaction. The presence of water and the alkaline conditions in the dyebath means that hydroxyl ions are present in solution and these compete with the cellulose as a nucleophilic reagent. This results in hydrolysed dyes which can no longer react with the fibre and accounts for the low levels of exhaustion achieved with some reactive dyes. Thus, between 10 and 50 % of the dye will be present in the effluent (Ends Report, 1993). For this reason, the project focused on the decolourisation of reactive dyes. An extensive literature review of structure and chemistry of reactive dyes is given in Annexure 3.

Initially, decolourisation of a one azo reactive dye was investigated. This dye was C.I. Reactive Red 141, the structure of which is shown in Fig. 1.2. This dye was chosen because (i) it is a reactive dye, (ii) it is an azo dye, the basis of which makes up approximately 80 % of the dyes used currently in the textile industry, and (iii) red is highly visible to the naked eye. This investigation was then extended to include other reactive dyes. The anaerobic decolourisation investigation expanded from laboratory to full-scale trials in the Pinetown region (Chapter 4, Section 4.6) and similar trials are being investigated in Hammarsdale (Chapter 4, Section 4.8). This project focuses on these two regions due to the co-operation of the textile industries in these towns and the support of the management of the waste water treatment plants.

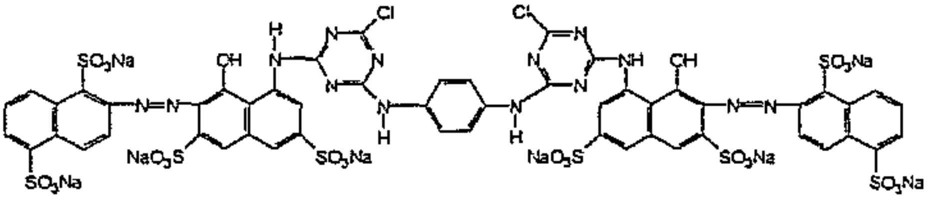


Fig 1.2 : Structure of C.I. Reactive Red 141.

In conjunction with the anaerobic study, the use of chemical reducing agents to decolourise azo dyes was investigated. Initial studies also concentrated on C.I. Reactive Red 141, but were extended to include other azo dyes. Analytical techniques such as thin layer chromatography (TLC), column chromatography, nuclear magnetic resonance spectroscopy (NMR) and high performance liquid chromatography (HPLC) were used to purify the dyes, confirm their structures and separate and identify the degradation products of the dyes. Some investigations into the use of electrochemistry to decolourise azo dyes have also been initiated.

In addition to investigating methods of removing the colour from textile effluents, waste minimisation surveys were conducted within the textile factories to promote good house keeping and process optimisation. This results in savings in water, chemicals and energy and reduces the effluent volume and load from the industries.

1.4 The Pinetown Region

The Umbilo Sewage Purification Works (USPW) in Pinetown discharges treated effluent to the Umbilo River. A detailed description of the treatment process is given in Annexure 10. The works receives both domestic and industrial effluents which, at the start of this project, included two large textile companies and two smaller ones. Insufficient colour removal was being achieved at the works with the result that coloured effluent was entering the Umbilo River and giving rise to a number of public complaints. It was felt that reactive dyes were the main cause of the problem and that red was the most problematic colour. Due to the increasing public pressure and stricter Department of Water Affairs and Forestry (DWAF) policies, the Borough of Pinetown was asked to implement steps to reduce colour from its discharge. This resulted in the formation of the Pinetown Colour Committee in May 1990, which consisted of representatives from the USPW, DWAF, the textile industries, the Water Research Commission (WRC) and the University of Natal. Explochem Water Treatment was commissioned to investigate methods of removing the colour either at the factory fence or at the USPW (Annexure 24).

The committee met for four years, during which time it was decided that no colour limit would be set for the discharge from USPW, but that it must not give rise to public complaints, and a limit of 400 ADMI was set for the textile industries. The Fenex process was found to be the most effective method of removing colour at the factories, both in terms of costs and results. Treatment plants have since been commissioned at the two larger textile industries. During this time, the USPW made available an anaerobic digester to the PRG in order to conduct full-scale trials into the feasibility of using anaerobic digestion as a treatment option. The details of this trial are given in Chapter 4. It was felt that although the trial was a success, too little information was available on the long term feasibility and the costs of transporting the effluent from the textile mill to the USWP were inhibitory.

1.5 The Hammarsdale Region

The Hammarsdale Waste Water Treatment Works (HWWTW) receives approximately 65 % of its flow from textile industries. Of the balance, 25 % is from a chicken abattoir and 10 % from domestic sources. A detailed description of the works and the effluent loads from the various industries is given in Annexure 11. The HWWTW discharges effluent into the Sterkspruit river in the Shongweni catchment area. A recent Receiving Water Quality Objective report prepared by Umgeni Water for the Sterkspruit / Shongweni system identified determinants in the final effluent from the works which were not complying with standards set by the DWAF. These include COD, conductivity and colour.

Although this research project was initiated to deal with the colour problems at the HWWTW, the implementation of the full-scale trials at the USPW, changed the focus of the research to Pinetown. Currently however, there are two research projects under investigation in the Hammarsdale region. These are discussed in detail in Chapters 4 and 6.

1.6 Project Aims

The main aims of the project were to :

- determine the fate of textile and specific industrial effluents through treatment processes;
- determine the effect of specific textile and industrial effluents on sewage treatment processes and on the quality of the final effluent;
- investigate the addition of polymers, flocculants or adsorbents at a sewage works to improve the removal of specific classes of pollutants;
- investigate the addition of processes within a sewage works to improve the removal of specific pollutants;
- investigate the treatment of specific concentrates which could be segregated at source;
- investigate the use of anaerobic digestion for the treatment of dye concentrates; and
- initiate an effluent monitoring and targeting programme at selected sites in order to minimise waste, reduce effluent load, predict the nature of the effluent and to target problematic streams.

This project was therefore initiated to investigate ways of treating textile effluents, either on-site or at the waste water treatment works, with the focus being on colour removal. In addition, waste minimisation and point source reduction techniques were to be introduced into the factories to reduce water, chemical and energy consumptions, thereby reducing the volume of effluent produced and making savings for the industry. At the same time, the importance of improving their environmental performance, such as replacing or eliminating chemicals classified as being harmful to the environment, was stressed.

The project was divided into three main sections, namely, biological and chemical treatment of textile dyes and effluent, and waste minimisation technology. **Chapter 2** presents a review of the available literature dealing with the biological and chemical treatment of dyes and textile effluents, and **Chapter 3** summarises the international legislation pertaining to the textile industry. Biological treatment focused on the use of anaerobic digestion to decolourise effluents and is discussed in **Chapter 4**. Chemical treatment investigated the use of reducing agents and various analytical techniques to separate and identify dye degradation products (**Chapter 5**). Some waste minimisation case studies are presented in **Chapter 6**. The conclusions of the project are given in **Chapter 7** and **Chapter 8** lists the various technology transfer achievements.

Chapter 2

Literature Review

This Chapter presents a summary of the available literature on the treatment of textile dyes and effluents and the toxicity of dyes and dye degradation products. Table 2.1 summarises the available textile effluent treatment options and Table 2.2 some of operational effluent treatment plants in various countries. A detailed literature review on the biological options for treating dye effluents and the proposed mechanisms of biological decolourisation is given in Carliell (1993) (Annexure 1). Annexure 5 gives a literature survey on the removal of textile dyes at wastewater treatment works. Each treatment stage at a conventional works was studied and the potential for colour removal at each point discussed. Naidoo (1994) (Annexure 2) presents a literature review of the chemical treatment options to treat dye effluents.

2.1 Biological Treatment Options

This section covers a discussion on the use of aerobic and anaerobic biological treatment systems, or a combination of the two, for the removal of colour from dye effluents.

2.1.1 AEROBIC DECOLOURISATION

An important property of textile dyes, which manufacturers and users have striven for, is resitance to oxidation. This explains why many dyes are resistant to oxidative microbial breakdown and therefore why conventional aerobic waste water treatment processes are ineffective in removing colour.

A number of researchers have investigated the use of activated sludge for the decolourisation of dyes. Flege (1970) studied the degradation of 4 disperse dyes and 3 reactive dyes. It was found that the disperse dyes were only partially degraded and the reactive dyes remained unchanged. It was thought that the anthraquinone-based dyes were converted to the unstable enol or leuco form. As part of a study by the United States Environmental Protection Agency (EPA) entitled *Fate of Water Soluble Azo Dyes in the Activated Sludge Process*, Shaul *et al.* (1988) investigated the partitioning of 18 water soluble azo dyes in the activated sludge process. Of these dyes, 11 compounds passed through untreated, 4 were adsorbed onto the sludge, and 3 seemed to be degraded. A study of the dye structures revealed that those that remained unchanged were highly sulphonated which was thought to prevent adsorption. The position of the substituents and the molecular mass of the dye also seemed to influence the reactivity, as the compounds that were adsorbed had higher molecular masses. It was suggested that sulphonation was a major factor in preventing azo dyes from being adsorbed or biodegraded, but that no definite conclusions could be drawn without a more in-depth study. As part of an on going study by the Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers (ETAD) into the environmental fate of dyestuffs, Pagga and Brown (1986), found that of 87 dyestuffs tested in the activated sludge process, none showed any significant biodegradation, although some solutions were substantially decolourised. This was attributed to adsorption of the dye onto the sludge. These results were also reported by Kulla (1981) when investigating the biodegradation of various synthetic organic colourants. They discovered that a certain amount of colour removal could be achieved through adsorption to sludge but that very little biodegradation takes place.

Therefore, in general, the activated sludge process does not have a great effect on textile dyes, especially water soluble dyes. These pass through the process untreated. Colour due to hydrophobic dyes (e.g. disperse, vat) is removed through adsorption to the biomass.

2.1.2 ANAEROBIC DECOLOURISATION

A number of studies have been carried out into the use of anaerobic digestion for the decolourisation of textile effluents. Flege (1970) investigated the anaerobic decolourisation of 3 disperse dyes and 2 reactive dyes. The sludge in the test with the disperse dyes became coloured, but the liquor remained unchanged. It was thought that the dyes were resistant to degradation under the test conditions. The reactive dye solutions were decolourised in 2 to 5 h. Analysis of the liquor (TLC) revealed that one of the reactive dyes (Reactive Violet 5) split into the 2 compounds from which it was synthesised, while the other (Reactive Blue 19) was degraded into 5 different coloured components, one of which was identified as Disperse Blue 19. It was proposed that the vinyl sulphone group had been removed.

A study of the anaerobic degradation of 22 soluble azo dyes was carried out by Brown and Laboureur (1983) as part of an ETAD project. The dyes were sent to 7 different laboratories together with Direct Red 7 as a control. The anaerobic sludges were obtained from either digesters at sewage works or from laboratory-scale digesters that had been fed to the correct requirements. The results showed that the 4 monoazo and 6 disazo dyes were significantly degraded in all laboratories, while the 2 poly azo dyes had inconsistent results varying in colour removal from 0 to 100 %. The results for 4 anthraquinone dyes varied from scarcely degraded to substantial degradation and the remaining 6 dyes had mixed results. The authors concluded that the majority of the dyestuffs tested showed a substantial degree of colour removal and that the degradation of dyestuffs in the environment is likely to be initiated under anaerobic conditions. In a following paper, Brown and Hamburger (1987) investigated the degradation of the dye metabolites formed during anaerobic digestion of selected azo, anthraquinone and phenoxazine dyes. It was found that a less than quantitative yield of the expected aromatic amines was obtained for the azo dyes. This was thought to be due to either impurities in the initial dyestuff, adsorption to the sludge, or that the expected mechanism (i.e. azo reduction) is not the only reaction that leads to decolourisation. These metabolites were not found to be further degraded in the anaerobic system.

The degradation of 2 monoazo dyes in serum bottles inoculated with sludge from an anaerobic digester was investigated by Kremer (1989). The rate of decolourisation was found to increase in the presence of supplemental carbon. Degradation was thought to occur through the reduction of the azo bond but no further breakdown of the metabolites was observed.

A study into the fate of the azo dyes Reactive Black 5 and Navy 106 (a mixture of 3 reactive dyes) was initiated by Ganesh et al., (1992). Under anaerobic conditions, a rapid decrease in the ADMI was observed with a change in colour from dark blue to greenish-yellow. It was proposed that this was due to the formation of aromatic amines resulting from azo bond cleavage. It was concluded that since complete elimination of the organic compounds does not occur, anaerobic digestion cannot be the final stage in the treatment of dye effluents.

An investigation into the feasibility of anaerobic digestion for the removal of colour from dyewastes was carried out by Churchley and Parkin (1984). Simple bottle tests were originally performed on both pure dyes and on dye effluent. It was found that most of the solutions were decolourised, with the exception of some xanthrene and triarylmethane dyes. Since these are not used to a great extent in the industry, it was not thought to be a drawback to anaerobic digestion. Experiments were also performed in continuous flow anaerobic columns and this method was found to decolourise dye effluent at retention times varying from 8 to 12 h. Two large-scale anaerobic columns were constructed to investigate the effect of surface area of the filter medium (90 and 60 m^2/m^3 respectively) on colour removal. Very little difference was found between the efficiencies of the columns, although for a given retention time, removal was greater in the column with the smaller surface area. It was concluded from this study that anaerobic digestion is a feasible route to take for the removal of colour from dyewastes, although the effects of the degradation products (aromatic amines) still needed investigation.

It is therefore generally accepted that azo dyes will be decolourised under anaerobic conditions. The mechanism involves the reductive cleavage of the azo bond to form the corresponding aromatic amines. This is a four electron process which proceeds through two stages. The first gives rise to an unstable, colourless compound which may revert to the original coloured form under oxidising conditions, or be further reduced under anaerobic conditions to form stable uncoloured compounds. These metabolites are not thought to be further degraded under anaerobic conditions. Anthraquinone and phthalocyanine dyes do not seem to be degraded anaerobically, probably due to the more stable structures.

2.1.3 COMBINATION OF ANAEROBIC AND AEROBIC BIOLOGICAL TREATMENT SYSTEMS FOR DECOLOURISATION

Since anaerobic treatment of dyes does not result in mineralisation of the degradation products and aerobic decolourisation does not seem to be effective, a two phase system combining an anaerobic stage for decolourisation with an aerobic stage for mineralisation of the degradation products has been investigated. Bhattacharya et al. (1990) reported 30 to 50 % dye removal in the anaerobic stage with a further 1 to 18 % in the aerobic stage. Unfortunately, the mineralisation efficiency could not be assessed.

Haug et al. (1991) reported complete decolourisation of the sulphonated azo dye, Mordant Yellow 3 under anaerobic conditions. The resultant aromatic amines were mineralised by aerobic micro-organisms. The use of a rotating drum biofilm reactor for the decolourisation and degradation of the azo dye Acid Orange 7 was investigated by Harmer and Bishop (1992). It was thought that by operating the reactor under aerobic bulk-liquid conditions that the biofilm would provide both anaerobic and aerobic zones. The results of this study showed that this system could be capable of both decolourising and mineralising azo dyes in a single stage.

It is therefore evident, that a combined anaerobic-aerobic system has potential as a treatment route for dye effluents.

2.2 *Chemical Analysis and Treatment Options*

This review summarises some of the available techniques for the analysis of dyes and the various physical and chemical treatment options.

2.2.1 IDENTIFICATION AND ANALYSIS OF DYES

Commercially available dyes are not pure and contain a number of other components; e.g. disperse dyes are usually 15 to 30 % pure and acid dyes approximately 50 % (Tincher and Robertson, 1982). The balance of the formulations contain substances such as dispersing agents, salts, sugar and other additives and reaction products. Therefore, it is necessary to have analytical techniques capable of separating, purifying and identifying dyes. Commonly used techniques include thin layer chromatography (TLC), nuclear magnetic resonance spectroscopy (NMR), ultra-violet light (UV), mass spectroscopy (MS) and, more recently, high performance liquid chromatography (HPLC) and high performance capilliary electrophoresis (HPCEP).

Traditionally, TLC has been used to separate mixtures of dyes. While it is a relatively fast and simple technique, it is not readily adaptable to analyses of large numbers of routine samples. The use of HPLC to separate and purify dyes has been investigated by a number of researchers. Briuns et al. (1987) showed that sulphonated dyes could be separated by HPLC and the fragments identified by MS. Schramm et al. (1988) developed a HPLC routine for the analysis of C.I. Reactive Red 4 at low concentrations and its derivatives. HPLC was also used by Maguire and Tkacz (1991) to identify 15 dyes present in the Yamaske River in Quebec downstream from textile industries. The use of HPCEP to analyse reactive dyes was described by Croft and Hinks (1992). They concluded that it was a more efficient technique than HPLC.

Naidoo (1995) (**Annexure 2**) investigated a number of techniques to analyse, purify and identify reactive dyes and their degradation products. The most effective method for separation and purification was found to be HPLC. The degradation products were identified by NMR.

2.2.2 CHEMICAL AND PHYSICAL TEXTILE EFFLUENT TREATMENT OPTIONS

The chemical treatment of textile effluents involves the use of either reducing or oxidising processes. Physical methods include adsorption, coagulation and membrane treatment.

Reduction methods : This involves the addition of strong reducing agents. In the case of azo dyes, decolourisation will result from the reduction of the azo bond and subsequent destruction of the chromophore. Nesyvona et al. (1984) describe the use of hydrosulphite to reduce an azo reactive dye.

Naidoo (1995) found that refluxing azo reactive dyes with stannous chloride resulted in decolourisation. The fragments identified where consistent with azo reduction.

Oxidative methods : These decolourise dyes by breaking down the dye molecule. Commonly used processes are ozone and the Fenton's Reagent.

Ozone has been investigated in a number of studies. It has been found that dye wastewaters react differently depending on the composition. Effluent containing sulphur and disperse dyes are difficult to decolourise whereas colour due to reactive, basic, acid and direct dyes is fairly easily removed. A study into the use of ozone for treating secondary effluent from a municipal plant treating dye effluent was performed by Stuber (cited by Beszedits, 1980). Substantial colour removal was achieved. The use of ozone after biological treatment in an activated sludge plant receiving municipal and textile wastes in Poland, decreased the COD and TOC and aided in colour removal (Beszedits. 1980).

In some regions of the United Kingdom, sewage treatment works receive large quantities of textile effluent and colour removal is a serious problem. The Leek Wastewater Treatment Works (Severn Trent Water Plc) currently uses ozone as a final treatment stage after the effluent has passed through an activated sludge plant. The plant is achieving substantial colour removal, but is not complying with the 100 percentile limit set by the National Rivers Authority. No evidence of toxicity due to ozonation has been detected. (Churchley et al.).

The main drawbacks with installing an ozonation plant are the high capital and operating costs. However improvements in generator and contacting equipment design, together with increasingly strict environmental legislation will probably lead to a more widespread application.

Fenton's Reagent consists of ferrous salt (usually sulphate) and hydrogen peroxide. The reaction is carried out at a pH of 3 and involves the oxidation of ferrous ion to ferric ion with the simultaneous production of the hydroxyl radical. This radical is a powerful oxidising agent and will attack organic compounds and cleave the bonds. In the case of dye molecules, this would lead to decolourisation.

A number of researchers have investigated the use of Fenton's reagent for the decolourisation of textile effluents, both simulated and real (Kuo, 1992; Ruppert et al., 1993; Gregor, 1990; Powell et al., 1992; Michelsen et al., 1992). A disadvantage (in terms of costs for the discharger) is the production of ferric hydroxide sludge, but it is thought that this sludge is advantageous to the biological treatment system (Gregor, 1990).

Physical methods : The mechanisms involved in physical treatment methods are based on the size or charge of the dye molecules. Examples are coagulation, membranes or adsorption.

Coagulation: De Haas et al. (1992) reported the use of alum at Hammarsdale Wastewater Treatment Works which receives approximately 70 % of its effluent from textile industries. The treatment works uses the 5-stage Bardenpho reactor system and the alum was added prior to the effluent entering the anaerobic zone. The optimum concentration was determined to be 150 mg/l. Alum dosing was initially implemented because the plant was not achieving sufficient phosphate removal and could not comply with the discharge standards, but it was found that in addition to decreasing the levels of phosphate to below the consent value, it also decreased the colour levels, although this did not always mean compliance with the colour standards.

Kertell and Hill (1982) describe the use of alum for removing colour from wastewater from a textile mill that processes mainly synthetic fabrics and uses mostly disperse dyes. The company treated its effluent in a series of aeration basins prior to discharge to river, but the existing treatment works was not complying with the standards set by the local department for colour, BOD and phosphate removal. The addition of alum to the effluent after the final aeration basin followed by sedimentation was effective in meeting the permit regulations. A study by Netzer and Beszedits (1978) into the use of lime as a coagulant for the treatment of textile effluent found that it was effective in removing most heavy metals and achieved a high degree of colour removal.

Adsorbents : The most commonly used adsorbent is activate d charcoal. It has been found to be effective in the removal of colour through the adsorption of dyes onto its surface (McKay and Sweeny, 1980; Netzer and Beszedits, 1978). The use of other adsorbents such as sawdust, peat, maize stalks, charcoal, sand, rice husks, peatmoss and vermiculite have been investigated for the removal of dyes from solution and have been found to achieve more than 50 % colour removal (Meyer et al., 1992). Waters cites a number of literature references where the adsorption of dyes onto silica gel, activated alumina, wood, clay and synthetic polymers has been successful. The use of macrosorb is discussed by Cockett and Webb (1995).

Membranes: Reviews on the use of membranes for the treatment of textile effluents are given by Buckley (1992), Crossley (1995) and Southern (1995). In general, nanofiltration or reverse osmosis are the most effective processes for removing colour and recovering water. The drawbacks of these processes are the high capital costs, the fact that the concentrated effluent still has to be treated and membrane fouling.

2.3 Combined Chemical-Biological Processes for Decolourisation

McCurdy et al. (1991) investigated the combination of chemical reduction with aerobic biological treatment to improve colour removal from textile effluents. The reducing agents investigated were sodium hydrosulphite, thiourea dioxide and sodium borohydrate. The effluent contained three azo reactive dyes. Sodium hydrosulphite was found to be the most effective with a 62 % colour removal. This effluent was then fed into a biological reactor, but it was found that the pre-treatment rendered the effluent inhibitory to biological treatment. This was overcome by adding an oxidising agent (hydrogen peroxide) after reduction.

The pre-treatment of textile effluent with oxidising agents such as ozone and Fenton's Reagent were investigated by Powell et al. (1992) and Michelson et al. (1992). Good colour removal was achieved in both cases, but it was not found to either improve or inhibit the subsequent biological treatment process.

2.4 Toxicity of Dyes and Dye Degradation Products

Due to the recalcitrant nature of dyestuffs in the activated sludge process, concern arose as to the toxicity of these compounds towards the micro-organisms. A screening method for determining the inhibitory effect of the dyestuffs on aerobic bacteria was developed by ETAD (Brown et al., 1981). Tests were performed on 202 dyestuffs and the results reported as the 50 % Inhibition Concentration (IC_{50}) values. Dyes from the direct, disperse, reactive, vat, mordent, pigment, acid and solvent ranges gave IC_{50} values greater then 100 mg/l thus indicating that they had no toxic effect towards the micro-organisms at the concentration expected in textile effluents. However, dyes belonging to the basic range gave IC_{50} values of less than 100 mg/l, which is in agreement with the results obtained by Ogawa et al. (1989) that basic dyes are inhibitory to micro-organisms. From these tests, and the general experience of ETAD, it was concluded that although dyes may cause concern at sewage works due to their colour, there should be no concern as to their toxicity. The exception to this ruling are the benzidine-based dyes, the manufacture of which is prohibited by ETAD members. This has resulted in some ETAD members resigning from the board (ETAD Annual Report, 1993).

Moll (1991) summarised the carcinogenic potential of dye degradation products. Information on the carcinogenic effect of dyes on animals was only available for a limited number of dyes, most of which were azo (approximately 70 % of all colourants on the market are azo dyes). The toxicity of these dyes was assessed in terms of azo separation, i.e. what aromatic amines are produced. This occurs through reduction of the azo bond or the influence of enzymatic systems. The main concern is for those azo colourants which can release carcinogenic amines during metabolism. In 1994 the German government banned the use of azo dyes that can be split into any of 20 listed amines (Turner, 1995). This applies to any consumer goods that remain in contact with the body for extended periods of time. While the majority of ETAD members do not manufacture or sell azo dyes affected by this regulation, there are some exceptions. ETAD has issued a statement in 1995 that all manufacturing companies must inform their customers whether they comply with these regulations. A review by Clarke and Steinle (1995) reports that although it is estimated that about 150 azo dyes currently commercially available would form, on reductive cleavage, an aromatic amine that is acknowledged to be an animal carcinogen, only about 15 of these aromatic amines are considered to be relevant to the colourant industry. In most cases, the reduction products of the azo dyes are aromatic aminosulphonic acids, which have little or no carcinogenic potential (Jung et al., cited by Clarke and Steinle, 1995).

Brown and Anliker (1988) summarise the effects of textile effluent on the environment and the toxicity with respect to fish and other aquatic organisms, sewage bacteria and plants. They concluded that due to the vast number of different dyestuffs and processes in which they can be applied, an accurate environmental risk assessment can only be made on individual dyestuffs and in individual dye-houses. A similar summary of research work initiated by the ADMI into the toxicity of dyes to aerobic and anaerobic bacteria and to fish is given by Vyas (1975).

Chapter 3

Environmental Legislation and the Textile Industry

3.1 Introduction

Growing awareness of environmental issues has resulted in comprehensive environmental legislation in developed countries. In contrast, many developing countries have little or no environmental legislation in place resulting in an ever increasing gap between the standards of environmental maintenance and protection achieved worldwide. This situation has resulted in developed countries instituting environmental quality criteria for products through a system known as ecolabelling, in this way discriminating against products (including imported products) that do not achieve these standards. Alternatively, international trade agreements are being signed which aim to maintain standards of environmental excellence, again discriminating against products / companies that do not conform. Clearly environmental issues are beginning to impact on international trade.

This chapter provides a brief overview of the international situation, with specific reference to the European Union (EU) and the United States of America (USA). A section has also been included on the South African Department of Water Affairs and Forestry's approach to water quality management and the impact on the South African industries. A more detailed discussion is given in *Annexure 6*.

3.2 The International Standards Organisation and Environmental Standards

In June 1993 a meeting was held in Toronto, Canada at which the International Standards Organisation (ISO) formally established a technical committee known as ISO/TC 207 : Environmental Management. More than 200 representatives, including South Africans, were present at the meeting. The number of participating countries (37 in total) is a reflection of the importance of this committee, which is currently the largest of all the ISO technical committees. Only 5 countries from the southern hemisphere are participating in these activities, of which South Africa is the only country from the African continent.

The International Technical Committee (ISO/TC 207) has identified seven areas of activity which need to be addressed and has appointed subcommittees for six of these and a working group for the seventh.

The South African Bureau of Standards (SABS), a founder member of ISO, is representing South Africa at ISO/TC 207 and is co-ordinating the South African participation. The SABS invited South African industry to participate in these activities and to nominate persons to act as convenors for local subcommittees, i.e. the local equivalent of the international sub-committees formed under ISO/TC 207. Each local convenor chairs the meetings of the local sub-committees and working groups and acts as the South African representative at the international sub-committee meetings. The convenors present the views and comments at international level of the local sub-committees and working groups. The following subcommittees have been formed by ISO/TC 207:

- environmental management systems;
- environmental auditing;
- environmental labelling;
- environmental performance evaluation;
- life cycle assessment/analysis;
- terms and definitions; and
- environmental aspects in product standards.

These are discussed in more detail in Annexure 6 together with the names of the South African representatives. The Pollution Research Group is represented on the local environmental labelling technical sub-committee by Ms S Barclay.

3.3 Charter of Fundamental Principles of Global Trade for Textiles and Apparel

A new set of international trade principles (May 1993) for the textile industry has been endorsed by clothing and textile trade associations and trade unions from the 12 member states of the European Union (EU); Austria; Switzerland; Sweden; Finland; Norway; the Czech Republic; the Slovac Republic; Japan; Canada; Mexico; Jamaica; and the USA.

A copy of this charter is included in Appendix 2 of Annexure 6.

Of particular interest is condition 7 :

> *Promotion of a world-wide positive approach to environmental issues aimed at overcoming unfair competitive advantages created by some countries failure to enact and enforce acceptable environmental standards. This means conditioning continued market access for goods on adherence to acceptable environmental practices in production of goods benefiting from such access.*

The signatories undertake to lobby government to adopt the charter of principles as the basis for the General Agreement on Tariffs and Trade (GATT) negotiations.

3.4 The European Union

The environmental legislation for textile finishing industries in the EU is discussed in two sections in Annexure 6. The first includes current or proposed EU legislation pertaining to liquid effluent from textile finishing industries and the second section discusses the development of ecolabels for textile products, the current status of textile ecolabelling in Europe and the proposed (draft) report for a pan-European ecolabel for textile products. This will be briefly summarised in this section.

3.4.1 EUROPEAN UNION WATER REGULATIONS

These regulations are divided into a number of categories :

- surface water intended for drinking water;
- treated drinking water;
- protection of the aquatic environment;
- groundwater protection; and
- urban wastewater.

Each of these contain directives which lay down limit values and quality requirements.

3.4.2 CURRENT LEGISLATION FOR DISCHARGE OF EFFLUENT FROM TEXTILE FINISHING INDUSTRIES.

Limits have been set by the EU for COD, pentachlorophenol (PCP), white spirits and colour.

COD : In the past little differentiation was made between biodegradable COD (usually measured as biological oxygen demand, BOD) and non-biodegradable COD. However, the EU Urban Wastewater Directive (91/271/EEC) stipulates that final effluent discharged from a sewage works into rivers will have a COD limit of 125 mg/l and a BOD limit of 25 mg/l. Thus, non-biodegradability will have a serious impact on future consents (limits), with an effluent that is poorly biodegradable being undesirable at a treatment works. As textile finishing effluents contain poorly biodegradable organic substances (auxiliaries and synthetic sizes and many textile dyes), textile industries may be subject to biodegradability limits on effluents, imposed by extended BOD tests or by BOD / COD ratio tests.

PCP : This is a substance which has been scheduled for release to water and its presence in effluent has to be restricted by law. Based on the EU directive most countries in Europe have adopted the limit value to compliance, which sets the limit of 2 000 µg/l. The exception to this is Germany which has introduced legislation to ban the use of PCP and the import of products containing PCP. The current river quality objective for PCP in UK rivers is an annual mean of 2 µg/l. Consents for the discharge of individual finishing works to a waste water treatment works are site specific (UK), usually about 20 µg/l, although some are as low as 6 µg/l.

White spirits : Emission to the air are strictly controlled. It must be noted that kerosene is listed as a hazardous compound and, according to the draft report for EU ecolabelling of textile products, cannot be considered for use as a binder / thickner for printing. No information was provided on discharge to sewer.

Colour : Although modern synthetic dyes are not considered to be toxic at the environmental concentrations usually encountered, colour in rivers and other natural water bodies is aesthetically displeasing, reducing the amenity value of the watercourses and affecting some industrial and potable abstractions. No definitive standards such as EU Directives or UK quality objectives exist on which to base river or effluent quality controls and, in the absence of toxicity the problem is largely aesthetic, increasing the risk of subjectivity.

3.4.3 ECOLABELLING IN THE EUROPEAN UNION

Ecolabelling schemes provide for the award of a label to products which meet specific objectives, thereby allowing the public to determine which products adhere to the environmental ratings stipulated in the regulations. Generally, the same criteria would apply to products manufactured in the country or to products imported into the country.

The European Union ecolabel award scheme was established by Regulation EEC No. 880/92, adopted on 23 March 1992. The regulation is directly effective in the laws of the EU member states and came into force on 2 May 1992. The regulation provides for the award of the ecolabel to products which meet the specified objectives :

- the products life cycle must have a *reduced environmental impact;*
- this must not compromise product or workers safety; and
- nor must it significantly affect the products fitness for purpose. Environmental benignity must not be bought at the cost of the product's efficiency.

An application for an ecolabel is made to the national competent body appointed by the government of each member state for that purpose. The body must be independent and neutral.

3.4.4 CURRENT AND PROPOSED ECOLABELLING SCHEMES IN THE EUROPEAN UNION

The EU working party on ecolabels for textile products is chaired by the Danish Environmental Protection Agency, with the current focus (product groups) being bed linen and T-shirts. A draft document has been produced for EU ecolabelling of textile products and is discussed briefly below.

The draft report was released in March 1993 and is presented in Appendix 3, Annexure 6 . The report is the result of work performed by an EU expert group and an EU *ad hoc* working group concerning development of ecolabelling criteria for textile products. At present the only products that have been investigated are T-shirts (lightweight weftknitted garment giving a T-shape when laid flat) and bed linen (sheets, duvet covers, pillow cases, and short-termed bed linen). Highlights from the report will be given here; a more detailed discussion is given in Annexure 6. There are four chapters; namely:

- **Chapter 1: Introduction.** introduces the concept of textile ecolabelling and describes the composition of the report. It highlights the methods used for developing ecolabelling criteria to clarify the remainder of the report
- **Chapter 2 : Key features.** Key features from all stages of the life cycle and covering all types of environmental aspects are described in relevant phases of the product life cycle. For each key feature preliminary proposals for use of chemicals, water, energy etc. are given, which are developed further in Chapters 3 and 4.
- **Chapter 3 : Impact assessment.** In this chapter the key features identified in Chapter 2 are selected and grouped according to the following list :
    - consumption of energy;

  - consumption of non-renewable resources;
  - consumption of renewable resources;
  - consumption of space (for waste disposal);
  - global aspects;
  - regional aspects;
  - local aspects; and
  - use of certain hazardous chemical products.
- **Chapter 4 : Conclusions and criteria proposal for T-shirts and bed linen made of 100 % cotton, 100 % polyester or blends of cotton and polyester.** The chapter is divided into 5 main sections relating to the sections described in Chapter 3. For each criterion proposed in the sections a short argumentation and conclusion for the selection of this particular criterion is given. The criteria system has some general provisions, e.g. that the product must always comply with the present EU regulations. In addition, the criteria consist of specific requirements, e.g. negative lists of excluded chemicals, hurdles and scoring systems. The proposed criteria cover raw materials, products, intermediates, additives, emissions, exposures etc.

A recent ENDS report (1995) reports that the eco-labelling criteria set out in this draft report have been toned down to gain the support of textile manufacturers. This new draft report was expected to be voted upon by the EC regulatory committee in June 1995. The following changes have been made :

- the product group has been extended to include other items made largely from cotton or cotton / polyester blends, e.g. sleepwear, towels and sweatshirts;
- the proposal focuses on only one stage of the textile life-cycle, namely, wet processing;
- limits on energy consumption during the production of polyester fibres and in mechanical processes such as spinning and knitting have been omitted;
- there is no criterion for colour in the effluent from wet treatment;
- many other criteria have been toned down, e.g. compounds or emissions that were banned in the initial report are now permitted to certain low levels; These include :
  - volatile organic compounds;
  - antimony catalysts;
  - heavy metals; and
  - formaldehyde;
- some additional criteria have been introduced and others tightened, for example:
  - biodegradability limits have been set for size;
  - limits on pH and temperature of the wastewater; and
  - bans the use of CFC's, HCFC's and PCP biocides throughout the textile life-cycle.

It is felt that a significant number of textiles would meet these criteria (Ends, 1995).

3.5 Water Quality Management in South Africa

3.5.1 OVERVIEW

South Africa is a water scarce country with an average annual rainfall of less than 60 % of the world average. It is therefore important for industries to minimise water consumption, and recycle and re-use water and effluent. The Department of Water Affairs and Forestry (DWAF) is responsible for the management of water resources in South Africa, thereby ensuring the provision of adequate water supplies of acceptable quality for all recognised users. From the quality point of view, recognised users are defined as: domestic, industrial, agricultural, environmental and recreational. Custodianship applies not only to inland ground and surface water resources, but also to South Africa's coastal-marine environment.

Until recently, the Uniform Effluent Standards approach to water pollution was implemented whereby compliance with the General and Special effluent standards was enforced. In order to counter deteriorating water quality in the country, two new approaches have been instigated; i.e. the Receiving Water Quality Objectives for non-hazardous substances, and the Pollution Prevention approach for hazardous effluents (Department of Water Affairs and Forestry, 1991).

3.5.2 UNIFORM EFFLUENT STANDARDS

This approach has been used for the past 3 decades and aimed to control the input of pollutants into the water environment by requiring that effluents comply with uniform standards such as the General and Special standards (Table 3.1). The advantages of this approach is that it is simple and easy to enforce and the standards can be frequently updated to incorporate the newest pollution abatement technology. There are a number of disadvantages to this approach, however, such as :

- it is focused on effluent and effluent treatment and ignores the effect on receiving water bodies; and
- there is no incentive for industries to locate at the most environmentally advantageous site.

This approach was successful in that it retarded the deterioration in water quality and focused attention on the prevention of pollution. The Water Act makes provision for exemption from the General Effluent standard. Relaxations of the standards for a specific period could be negotiated, but these were based on technological and economical considerations and did not take into account the impact on the receiving water quality.

Table 3.1 : Special and General Effluent Standards

	Special Standard	General Standard
Colour, odour, taste	no detectable colour, odour or taste	no detectable colour, odour or taste
pH	5.5 to 7.5	5.5 to 9.5
Dissolved oxygen (%)	> 75	> 75
Typical (faecal) coli (per 100 ml)	none	none
Temperature (°C)	< 25	< 35
COD (mg/l)	< 30	< 75
OA (mg/l)	< 5	< 10
Conductivity (mS/m)	< 15 % above intake water	< 75 mS/m above intake water
Suspended solids (mg/l)	< 10	< 25
Sodium (mg/l)	< 50 above intake water	< 90 above intake water
Soap, oils, greases (mg/l)	none	< 2.5
Other constituents : (in mg/l)		
residual chlorine (CP)	Nil	0.10
free and saline ammonia (N)	1.00	10.00
nitrates (N)	1.50	-
arsenic (As)	0.10	0.50
boron (B)	0.50	1.00
total chromium (Cr)	0.05	0.50
copper (Cu)	0.02	1.00
phenolic compounds (as phenols)	0.01	0.10
lead (Pb)	0.10	0.10
soluble ortho phosphates (P)	1.00	-
iron (Fe)	0.30	-
manganese (Mn)	0.10	0.40
cyanide (CN)	0.50	0.50
sulphides (S)	0.05	1.00
fluoride (F)	1.00	1.00
zinc (Zn)	0.30	5.00
cadmium (Cd)	0.05	0.05
mercury (Hg)	0.02	0.02
selenium (Se)	0.05	0.05

However, even with these standards, the water quality in South Africa continued to deteriorate and DWAF was forced to re-evaluate its approach to water pollution. For these reasons, the Receiving Water Quality Objectives and Pollution Prevention approaches were introduced.

3.5.3 RECEIVING WATER QUALITY OBJECTIVES APPROACH

This approach takes into account that the receiving water has the ability to assimilate pollution with no notable detriment to the water quality requirements of the recognised users. This has resulted in :

- the compilation of water quality guidelines based on the requirements of the recognised uses;
- the formulation of water quality management objectives based not only on the requirements of the users, but also on economic, social, political, legal and technological considerations; and
- the imposition of site-specific effluent standards to ensure that the water quality objectives are met for that particular receiving water body.

Fundamental to this approach is a knowledge of the quantity and quality of water required by the different sectors.

The advantages of this approach are that both point and non-point sources are taken into consideration and it encourages industries to locate in areas where they will have a reduced environmental impact. The disadvantages from a regulatory perspective are that it is technologically more demanding as a knowledge of the chemistry of the pollutants is required, and more detailed investigations are necessary in order to compile a site-specific effluent standard than is required for the special standards.

In general, DWAF follows the *polluter pays principle*, whereby polluters are increasingly required to treat their effluents, and undertake and fund monitoring programmes and ecological impact studies to assess the environmental effects of their discharge.

3.5.4 POLLUTION PREVENTION APPROACH

This approach is aimed at the handling and disposal of hazardous wastes as toxicity, persistence and capacity for bioaccumulation present major threats to the environment. It involves source reduction and recycling to reduce the quantity and / or toxicity of waste and to minimise both present and future threats to the environment and public health.

3.5.5 WATER QUALITY MANAGEMENT

Much of the DWAF policy on water management focuses on anticipatory environmental protection, whereby preference is given to controlling the causes of pollution rather than trying to treat the symptoms. This implies that industries are required to reduce emissions to the environment through adopting the best available technology to control pollution and promoting conservation and efficient use of resources.

The Department is currently following a hierarchy of water quality management goals as follows :

- Source reduction, recycling, detoxifying, neutralisation etc. of wastes are required.
- If effluent must be discharged, it must meet the minimum effluent standard which can be either uniform or industry-based. (The current Special ans General Effluent Standards has been adopted, for the time being, as the minimum effluent standard).
- If the minimum effluent standards is insufficient to maintain the fitness of the receiving water body, then more stringent standards are enforced.
- Exemptions from effluent standards are considered only as a last resort provided the receiving water has available assimulative capacity. Exemptions must be justified on a technological, economical, environmental and socio-political basis.

Water quality management objectives are developed based on specific user requirements and, therefore, a good understanding of these requirements is essential. As mentioned previously, five main water users have been identified; i.e. domestic, recreational, industrial, agricultural and natural environment, and water which might be fit for use in the one specific group may not be suitable for another.

In order to determine whether water is fit for use, it is necessary to establish if the presence or introduction of any material into the resource would interfere with the intended water use. It is therefore important to have a yardstick against which to measure the effect of changes in the water quality. For this reason, water quality guidelines were compiled for each specific sector.

In the industrial sector, only those industries that use large volumes of untreated water were considered. These industries included :'

- leather and tanning
- power generation
- iron and steel
- pulp and paper
- petrochemical
- textiles

3.5.6 AIDE MEMOIR FOR INDUSTRIAL USE AND DISPOSAL

An Aide Memoir has been issued by DWAF to aid industrialists in preparing a water quality management report to support the application for permits and exemptions for industrial use and disposal (see Appendix 5, Annexure 6). It provides a list of items to be considered when drawing up a water quality management report (WQMR). The report submitted by the industry must include the following :

- brief project description, e.g. company name, address, magisterial district, nature of activity, annual production and reason for application;
- description of the environment, e.g. climate, land capacity, natural vegetation and plant life, surface water, groundwater, air quality, regional socio-economic structure and interested and affected parties;

- motivation for the project and works, e.g. benefits, where product will be sold, size of labour force and annual expenditure;
- industrial water use and process description, e.g. source of water, monthly quantities required, number of production days, water rights, processes in which water is used, raw materials, process description and final product description;
- industrial processes and re-use options, e.g. process descriptions, raw effluent produced, effluent re-use options and various effluent purification processes options;
- production, nature and disposal of industrial liquid and solid waste, e.g. quantity of waste, analysis of waste, effluent treatment works, disposal procedures and destination (land, river etc.);
- Purification of domestic sewage component of industrial undertaking (only if sewage is not sent to sewage works)
- Water and material balance diagram;
- WQM and pollution prevention methods, e.g. description of hierarchy of staff and availability of staff, WQ operational plan and description and analysis of technology used;
- pollution prevention and stormwater management;
- disposal of domestic effluent and solid waste;
- final effluent disposal evaluation, i.e. an in-depth analysis of all waste and the method of disposal;
- recommendations from other interested parties, e.g. Department of National Health and Population Development, Department of Environment Affairs, Nature Conservation Bodies, Department of Agriculture, Interested and Affected Parties, etc.

These requirements are described in more detail in Annexure 6, Appendix 5 of this report.

3.5.7 WATER QUALITY GUIDELINES FOR WATER USE IN THE TEXTILE INDUSTRY

The target guidelines for water quality requirements for the textile industry are given in Table 3.2. The effect of any deviations from these guidelines could have implications on the cost of producing textiles, technology of producing textiles, supervision and waste and effluent handling problems (Department of Water Affairs and Forestry, 1993).

3.5.8 EFFLUENT PRODUCED BY THE TEXTILE INDUSTRY

Of the industrial effluents, those produced by the textile industry are considered the most problematic as they are highly coloured and have high COD and conductivity. The majority of textile industries in South Africa discharge to sewer and their effluents must therefore comply with limits set by the local authorities (who in turn, have to compy with the requirements set by the DWAF).

Table 3.2 : Water Quality Guidelines for the textile industry

Parameter	Guideline
pH	7.0 to 8.5
Conductivity	10 to 70
Suspended solids	0 to 5
Total hardness	0 to 25
Alkalinity	0 to 100
Sulphate	0 to 250
Chloride	NS
Iron	0.0 to 0.2
Manganese	0.0 to 0.1
COD	0 to 10

3.5.9 PROSECUTION

The Water Act makes provision for the prosecution of offenders that do not comply with its regulations. The maximum penalty for a first time offender is R 50 000 and / or one year imprisonment. This is increased to R 100 000 and one year imprisonment for second offenders. Additional penalties may be applied if deemed necessary. It has been the DWAF policy not to prosecute offenders immediately. DWAF, however, due to continual deterioration in the quality of the RSA water resources, consider pollution as a serious offence and are therefore prosecuting offenders immediately.

The previous DWAF approach of results through negotiation wasz successful with a number of the textile industries in the kwaZulu-Natal region. For example, in Pinetown where there were numerous public complaints of colour in the Umbilo River, the DWAF, together with the local municipality and the textile industries, managed to find a solution through the formation of the Pinetown Colour Committee (Annexure). Similar success stories are being achieved at textile mills on the kwaZulu-Natal South Coast and one on the kwaZulu-Natal North Coast which discharges directly to sea.

Chapter 4

Anaerobic Decolourisation

4.1 Introduction

The objectives of this section of the research project was to investigate the feasibility of biological anaerobic treatment for the decolourisation of textile dyes, with respect to the mechanism and rate controlling factors of decolourisation, and the fate of the dye metabolites in an anaerobic system. As mentioned previously, this work was initially carried out on a laboratory scale using a specific azo reactive dye, C.I. Reactive Red 141. These investigations were then extended to investigate the decolourisation of a range of reactive dyes. Full-scale trials at the Umbilo Sewage Purification Works (USPW) in Pinetown were conducted and preliminary investigations are under way to carry out a similar trial at the Hammarsdale Waste Water Treatment Works (HWWTW). In addition, the feasibility of combining the treatment of the high COD textile finishing streams (e.g. desizing, scouring and bleaching) with the decolourisation of C.I. Reactive Red was investigated on a laboratory scale with the aim of developing a combined systems for on-site textile effluent treatment.

4.2 Decolourisation of C.I. Reactive Red 141

The rate of decolourisation of C.I. Reactive Red 141 under anaerobic conditions was investigated with respect to :

- the effect of prior exposure of the biomass to the dye;
- the initial dye concentration;
- additional carbon source requirements;
- the presence of additional electron acceptors;
- the redox potential of the system; and
- adsorption to the biomass.

The identification and fate of the degradation products as well as the toxicity of these metabolites and the parent dye molecule to the biomass was also investigated. The details of the experimental work is given in Annexure 1. In all experiments, decolourisation was measured by determining the absorbance of the solution at the wavelength of maximum absorbance of the dye (520 nm). This was converted to concentration by using a calibration curve.

4.2.1 THE EFFECT OF PRIOR EXPOSURE OF THE BIOMASS TO THE DYE

Adaptation of a microbial population to degrade a previously recalcitrant compound, through prior exposure of the micro-organisms to this compound, is known as enrichment or acclimation. It has been reported in literature that although anaerobic decolourisation of textile dyes does occur with unacclimated biomass, Meyer (1981) reported that enriched biomass can enhance the rate of degradation.

The first step in this experiment was a four month enrichment period, where biomass was exposed to C.I. Reactive Red 141 starting at a dye concentration of 10 mg/l and increasing at monthly intervals to give a final concentration of 200 mg/l (cumulative concentration). This enrichment was performed with the aims of :

- Improving the rate of decolourisation;
- Improving degradation and possibly minerilisation of the dye degradation products; and
- Improving microbial tolerance to inhibitory concentrations of the dye and/or dye degradation product.

Serum bottle experiments were performed using this enriched biomass and biomass that had not been previously exposed to the dye. The results showed that although prior exposure of the biomass to the dye did not increase the rate decolourisation, it did increase the resistance of the micro-organisms to concentrations of the dye that were found to be inhibitory to the unacclimated biomass. The experiments to investigate the effect on mineralisation were inconclusive, but it was thought to be unlikely that further degradation of the metabolites would occur under anaerobic conditions.

The enriched biomass was used in all further experiments unless otherwise stated.

4.2.2 INITIAL DYE CONCENTRATION

These experiments were also performed in serum bottles. Initial dye concentrations of 100, 150 and 200 mg/l were used. The rate of decolourisation of C.I. Reactive Red 141 was found to be inversely proportional to the initial dye concentration as shown in Fig 4.1. This was attributed to the accumulation of toxic metabolites in the system at the higher concentrations.

4.2.3 ADDITIONAL CARBON SOURCE REQUIREMENTS

The rate of decolourisation C.I. Reactive Red 141 was measured in the presence of an additional carbon source (glucose) and compared with decolourisation rates with the dye as the sole carbon source. The results are shown in Fig 4.2. As can be seen, the rate was enhanced in the presence of glucose. There were

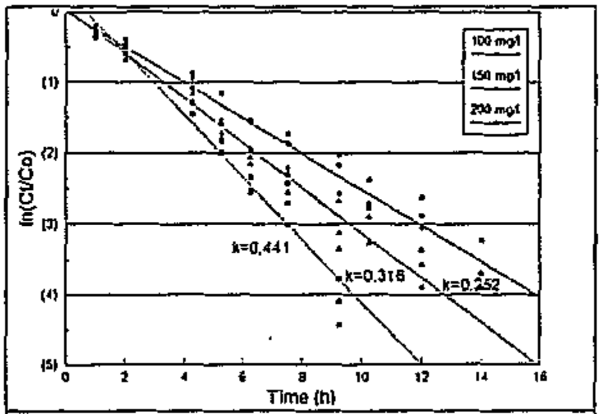


Fig 4.1 Decolourisation rates for C.I. Reactive Red 141

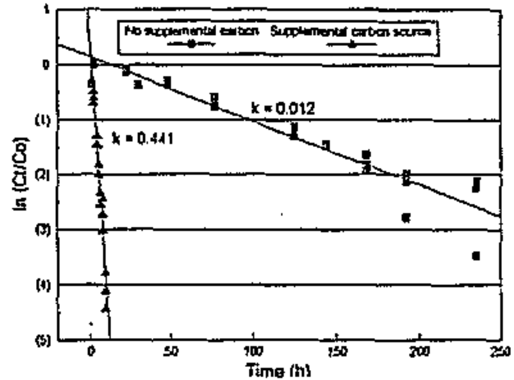


Fig 4.2: Decolourisation rates for C.I. Reactive Red 141, with and without the addition of glucose.

a number of possible explanations for this observation, the one thought to be the most feasible was that the presence of glucose enhances the rate of formation of reduction equivalents, i.e. reduced flavin nucleotides.

4.2.4 THE PRESENCE OF ADDITIONAL ELECTRON ACCEPTORS

As reduction (decolourisation) of C.I. Reactive Red 141 occurs via an electrochemical reduction mechanism in which the dye is utilised as the terminal electron acceptor in the microbial electron transport chain, the presence of other electron acceptors could be rate-limiting. The presence of nitrate in the anaerobic system was found to retard decolourisation for a period of time proportional to the concentration of nitrate present (see Fig 4.3), however, addition of sulphate was found to have no effect on the rate of decolourisation. It was, therefore, postulated that the preferential order of reduction would be nitrate > C.I. Reactive Red 141 > sulphate, and that decolourisation was dependent on the redox potential of the dye.

4.2.5 THE ROLE OF REDOX POTENTIAL IN AZO REDUCTION

The results in the previous section led to the investigation of polarography as a means of determining the potential at which C.I. Reactive Red 141 would be reduced. It was thought that this technique would be a

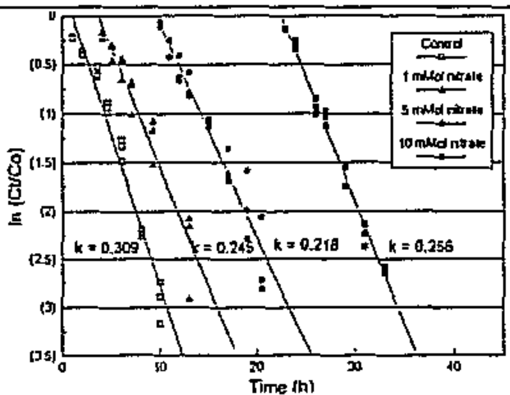


Fig 4.3: Decolourisation rates for C.I. Reactive Red 141 in the presence of nitrate.

quick and simple method of screening various dyes to determine whether they would be susceptible to anaerobic digestion. The experimental work performed on C.I. Reactive Red 141 by means of a dropping mercury electrode is detailed in Annexure 7. Solutions of the dye were prepared in buffers ranging in pH values from 1 to 12. The initial results seemed to indicate that C.I. Reactive Red 141 was being reduced at the electrode and following the same mechanisms described in literature. However, it was found that these curves were indicative of the reduction of oxygen in water and not of the reduction of the dye. Samples were therefore purged with nitrogen for longer periods of time. This resulted in an elimination of the curves previously obtained, but no meaningful results were obtained. Even changing the electrolyte to potassium chloride gave no improvements. Other electrochemical methods were employed such as cyclic voltammetry and DC stripping, but again, no curves indicative of reduction were obtained. It was suggested that the dye molecule was too large to diffuse to the electrode and was therefore not being reduced.

Since this method proved unsuccessful for the determination of the redox potential of C.I. Reactive Red 141, it was suggested that the redox conditions of the anaerobic digester be monitored during decolourisation trials. In order to achieve this, electrodes were inserted into the digester and connected to a computer which recorded the potential at various intervals. The effect of the presence nitrate and sulphate on the redox potential could therefore be determined.

Continuous redox potential measurements of an anaerobic digester were undertaken when C.I. Reactive Red 141 was present as a sole electron acceptor, or in conjunction with nitrate or sulphate. Fig 4.4 shows that decolourisation of C.I. Reactive Red 141 alone occurs at a redox potential, relative to saturated calomel electrode, of approximately -450 mV (SCE) and is completed within 5 h of addition. Fig 4.5 shows that the redox potential of a digester containing nitrate and C.I. Reactive Red 141 is initially low (-450 mV, SCE) but rapidly increases to a plateau at approximately -220 mV which is thought to concur with nitrate reduction in the system. During this plateau of increased redox potential no decolourisation of the dye occurs, however, once the redox potential drops to approximately -450 mV (SCE) decolourisation proceeds rapidly. Thus, it may be concluded that strong reducing conditions are favourable for rapid decolourisation of the dye and any interfering electron acceptors would have an inhibitory effect on the decolourisation process. This is of great practical significance as both nitrate and sulphate salts are commonly used in reactive dyeing.

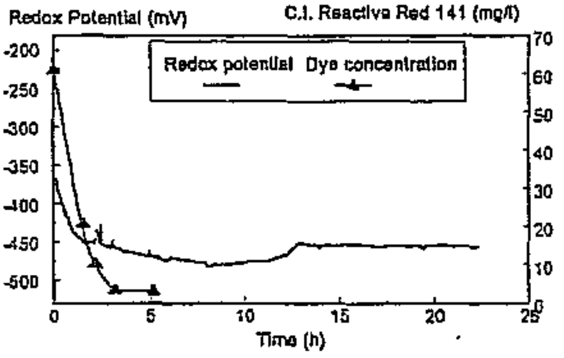


Fig 4.4 : Redox potential (SCE) measured in an anaerobic digester during decolourisation of C.I. Reactive Red 141 (100 mg/l)

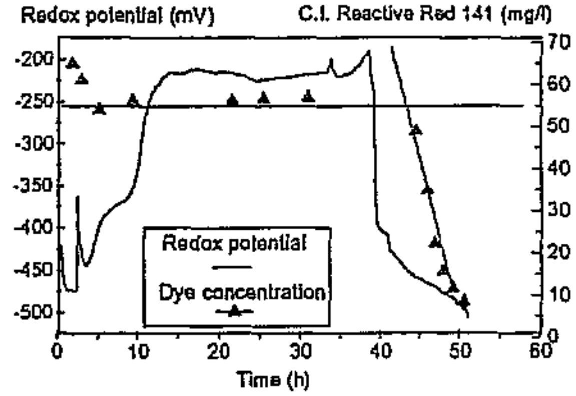


Fig 4.5 : Redox potential (SCE) measured in an anaerobic digester containing nitrate (20 mM) and C.I. Reactive Red 141 (100 mg/l).

4.2.6 ABIOTIC DECOLOURISATION

Although reactive dyes such as C.I. Reactive Red 141 are extremely water-soluble, it is necessary to determine the amount of dye that is removed from the anaerobic system via adsorption to the biomass. Adsorption isotherms (with C.I. Reactive Red 141 as the adsorbate and biomass as the adsorbent) showed a monolayer adsorption pattern, i.e. saturation of the adsorbent occurred at relatively low solute concentrations, with the amount of dye adsorbed reaching a maximum value at moderate concentrations (17 to 20 mg/l). Linear relationships were obtained when this data was represented by both the Langmuir and Freundlich equations. Experiments were then conducted to determine the fate of the adsorbed dye. It was found that the dye was subsequently decolourised, and therefore, no distinction was made between biological and abiotic decolourisation in all experiments.

4.2.7 INHIBITORY EFFECTS OF C.I. REACTIVE RED 141 IN AN ANAEROBIC MICROBIAL POPULATION

A toxicity assay was performed to determine whether increasing concentrations of C.I. Reactive Red 141 would be inhibitory to the anaerobic biomass. Fig 4.6 shows the results obtained with dye concentrations ranging from 20 to 500 mg/l. A maximum rate ratio (MRR) between 0.95 and 0.90 indicates possible inhibition, whereas one below 0.9 indicates significant inhibition. It can be seen that prior-exposure biomass, i.e. that exposed to C.I. Reactive Red 141 during the enrichment programme, exhibits a greater resistance dye inhibition than the unacclimated biomass. This suggests that a dedicated treatment system could adapt over time to treat and decolourise increasingly concentrated textile waste waters.

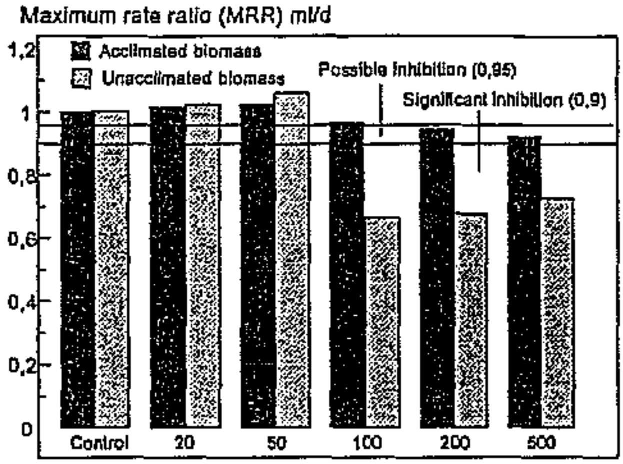


Fig 4.6: Maximum rate ratio's for anaerobic toxicity assay with C.I. Reactive Red 141(for dye concentrations ranging from 20 to 500 mg/l)

4.2.8 THE IDENTIFICATION AND FATE OF C.I. REACTIVE RED 141 DEGRADATION PRODUCTS IN AN ANAEROBIC SYSTEM

In order to confirm that decolourisation of C.I. Reactive Red 141 occurred via azo reduction, ultraviolet scans were performed on the digester supernatant before, during and after decolourisation. The ultraviolet scans showed a peak in the visible region of the spectrum before the onset of decolourisation which was reduced during the decolourisation process, indicating that cleavage of the azo bonds had taken place. Azo bond cleavage was also confirmed by separation and identification of 2-aminonaphthalene-1,5-disulphonic acid (see Chapter 5, Fig 5.1) which was formed as a result of azo reduction.

The fate of these degradation products in the anaerobic system was investigated during a 52 d serum bottle mineralisation test. The test indicated that no *ready* mineralisation of the degradation products would be expected in the anaerobic system which gave rise to decolourisation. (as determined by measuring gas production over the 52 d period). This is supported by the literature and can be attributed largely to the presence of sulphonate groups on the dye compound which are only removed under strictly aerobic conditions.

4.3 Anaerobic Digestion of a Range of Reactive Dyes

The laboratory-scale anaerobic decolourisation study was then extended to include a range of reactive dyes commonly used in both the dyeing and printing of cellulosic fabrics (Annexure 8 and Annexure 13). The predominant chromophore class was azo, although phthalocyanine and anthraquinone dyes were included in the test. The primary biodegradability, i.e. decolourisation of 18 reactive dyes was investigated using the same serum bottle techniques as was used for C.I. Reactive Red 141. Table 4.1 shows the results obtained with the spectrum of dyes. With the exception of C.I. Reactive Yellow 95, all the azo dyes tested were decolourised by 70 to 90 %. The three phthalocyanine dyes tested gave a wide spread of results with decolourisation efficiencies ranging from 25 to 90 % and the anthraquinone dye showed little decolourisation.

Table 4.1 : Results obtained when incubating selected reactive dyes in an anaerobic system with supplemental carbon.

	Chemical classification	Percentage decolourisation	Reaction time (h) required to attain maximum decolourisation.
Reactive dye powders			
C.I. Reactive Yellow 16	azo	80 to 90	6.5
C.I. Reactive Red 198a	azo	85 to 90	2.0
C.I. Reactive Red 141	azo	85 to 90	4.5
C.I. Reactive Blue 38	phthalocyanine	40.0	4.5
C.I. Reactive Blue 21	phthalocyanine	85 to 90	4.5
C.I. Reactive Blue 220	azo	90 to 95	1.0
C.I. Reactive Black 5	azo	80 to 85	4.5
Reactive dye solutions			
C.I. Reactive Yellow 95	azo	0.0	-
C.I. Reactive Orange 12	azo	90 to 95	23.0
C.I. Reactive Red 218	azo	90 to 95	32.0
C.I. Reactive Red 24	azo	95 to 97	32.0
C.I. Reactive Orange 13	azo	85 to 90	50.0
C.I. Reactive Brown 11	azo	90.0	23.0
* Reactive Blue PB	metal complex	98	2.0
C.I. Reactive Blue 49	anthraquinone	7 to10	2.0
C.I. Reactive Black 39	azo	70 to 75	5.5
* Reactive Black SG	metal complex	75 to 80	7.5
C.I. Reactive Blue 72	phthalocyanine	25 to 30	50.0

* No C.I. number available

4.4 Anaerobic Digestion of Cotton Finishing Effluents in Combination with Decolourisation of C.I. Reactive Red 141

As discussed in Section 4.2.3, anaerobic decolourisation of C.I. Reactive Red 141 required the presence of supplemental labile carbon to maintain the anaerobic microbial population in an active state. Laboratory studies used glucose as a carbon source, however this would not be feasible on a large industrial scale. Therefore, the enrichment of biomass which was capable of degrading the organic content of a cotton scouring effluent was investigated (Annexure 1). It was found that this microbial population was able to decolourise C.I. Reactive Red 141 while digesting the scour effluent organics, giving rise to a final effluent with reduced COD, pH and colour. Decolourisation was found to be first-order with respect to dye concentration, and to be inhibited by the presence of nitrate in the feed. This research shows the possibility of combining energy-rich and highly coloured textile effluents in an anaerobic digester with the aim of reducing the effluent COD, pH and colour.

4.5 The Fate of C.I. Reactive Red 141 in a Conventional Wastewater Treatment Works

The results of this experiment are reported in detail in Annexures 9 and 13.

Based on the success of the laboratory decolourisation trials, it was decided to investigate the decolourisation of C.I. Reactive Red 141 in a conventional sewage treatment works. A mass of the dye (calculated to be typical of a dyebath drop), was dosed into the Hammarsdale Waste Water Treatment Works (HWWTW) during the shut-down period of the textile industries in the area. The progress of the dye through the works was predicted from residence time distribution curves obtained by entering the flow, concentration and volume parameters into IMPULSE (Baddock, 1992), sampling at various time intervals. It was observed that after 30 min there was no visual colour in the samples. A scan in the visible region of this sample and of a blank taken prior to addition of the dye, appeared to be identical. It was therefore concluded that (i) the dye was being decolourised by the bacteria, (ii) it was being adsorbed to the sludge, or (iii) the dilution factor was too great for any colour to be visible. In order to determine the cause of decolourisation, laboratory scale tests were performed on mixed liquor samples taken from the anaerobic and anoxic zones of the reactor and dye was added to give the same dilution factor as dosed in the reactor. Decolourisation was monitored by measuring adsorption at the wavelength of maximum absorbance of C.I. Reactive Red 141. From these results, it was concluded that the dye was decolourised by the bacteria, as colour was visible in the samples and no initial rapid decolourisation occurred, which would have been indicative of adsorption. A graphical summary is given in Fig 4.7.

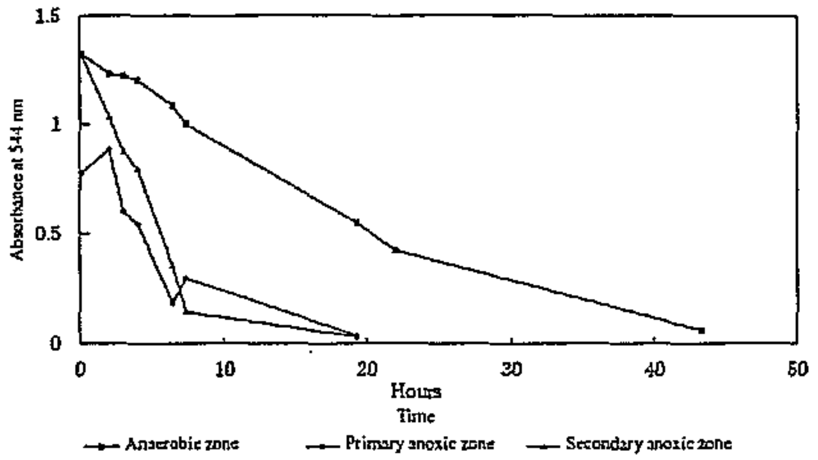


Fig 4.7: Decolourisation of C.I. Reactive Red 141 under anaerobic and anoxic conditions.

4.6 Co-treatment of Concentrated Reactive Dyebath Effluent in an Anaerobic Sludge Digester - Full-scale Trials

Due to the success of the laboratory studies and the tests at HWWTW, it was decided to investigate the anaerobic treatment of concentrated dye bath effluent. An alternative to using scour effluent as a carbon source is to use the reducing powers of an established anaerobic system, such as a digester at a sewage works. The feasibility of this process was investigated at the USPW in Pinetown over a five month period in 1994, the details of which are given in Annexure 4.

The USPW allowed the use of one of their four heated primary digesters for this investigation. The trial began at the end of May 1994 and continued for 5 months. Concentrated dyebath effluent was obtained from Ninian and Lester in Pinetown, where the reactive dyebaths from yarn dyeing were pumped to a 5 Kl storage tanks fitted with an overflow. The effluent was trucked to the treatment works on a daily basis (Monday to Friday) and discharged into the empty sump at the primary sludge pump station. The digester chosen for the trial (digester 2) was isolated from the other digesters and the dye effluent pumped to this digester. Digester 3, which received no dye effluent was used as the control. On average, 3 Kl/d was trucked to USPW. The digesters were fed 4 times per day with raw sludge from the primary settling tanks, sludge from the trickling filters and waste activated sludge. Details of the USPW are given in Annexure 10.

A laboratory-scale digester was run in conjunction with the full-scale trial in order to simulate the conditions in the primary digester. Innoculum for the laboratory digester was obtained from digester 2. The laboratory digester was fed every morning with raw sewage from the plant. Once the digester had stabilised (10 d), dye effluent was added to the digester each day (Monday to Friday) after the feed. It was dosed at approximately 1.5 times the dye load of the full-scale digester.

4.6.1 SAMPLE ANALYSIS

Samples of the dye effluent were kept for ADMI analysis and sodium and sulphate concentration. An analysis of the dye effluent added to the digesters is given in Annexure 4, Appendix A. Samples of the overflow from digesters 2 and 3 and the laboratory digester were collected daily after the morning feed. These sludge samples were analysed for total solids and volatile solids, and were centrifuged to analyse the supernatant for pH, alkalinity, volatile acids, and sodium and sulphide concentration. These results are given in Annexure 4, Appendix C (full-scale digesters) and Appendix D (laboratory digester). In addition, the supernatant was filtered for ADMI analysis, but difficulties in obtaining clear samples was experienced.

4.6.2 RESULTS AND DISCUSSION

As the ADMI analyses were unsuccessful, a visual comparison was made between the supernatant of digester 2 and the laboratory digester and that of digester 3, and since no difference in colour was observed, it was concluded that decolourisation of the dye effluent was occurring.

High levels of sodium and sulphide concentrations were recorded in both the full-scale and laboratory digesters. These results are shown in Figs 4.8, 4.9, 4.10 and 4.11. The vertical lines in Figs 4.10 and 4.11 indicate the time period over which the dye effluent was added to the laboratory digester.

These high levels of sodium and sulphide were attributed to the high concentration of sodium sulphate used in the reactive dyeing process (typically 80 g/l) as sulphate is reduced to sulphide under anaerobic conditions (this relationship is shown in Fig 4.11). In addition, the levels of sodium and sulphide in digester 2 were consistently higher than that of digester 3 (Figs 4.8 and 4.9).

While the levels of sodium in both the full-scale (0.786 g/l) and laboratory digester (1.5 g/l) were below the concentration reported in literature to be inhibitory to methanogenesis (between 3.5 and 5.5 g/l, Kugelman and McCaerty, 1965; cited by De Baere, 1984), increasing the dye effluent load may result in cation toxicity.

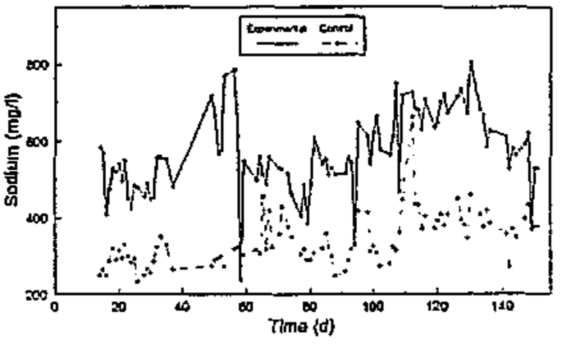


Fig 4.8: Sodium concentrations in digesters 2 and 3.

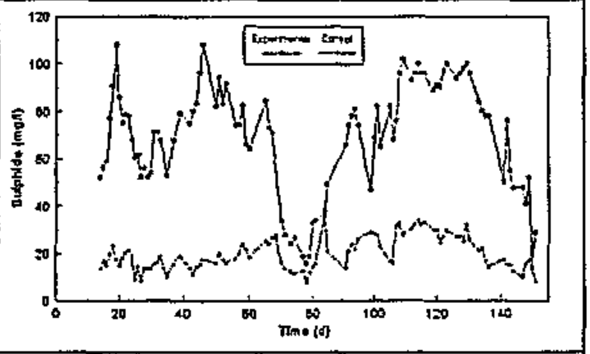


Fig 4.9: Sulphide concentrations in digesters 2 and 3.

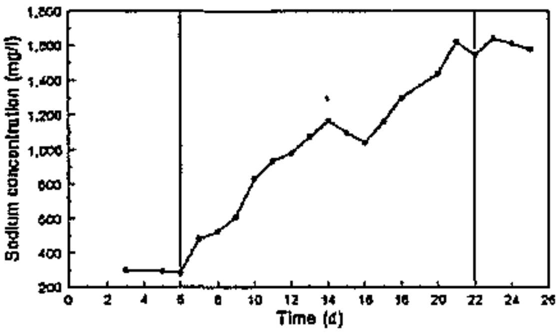


Fig 4.10: Sodium concentrations in the laboratory digester

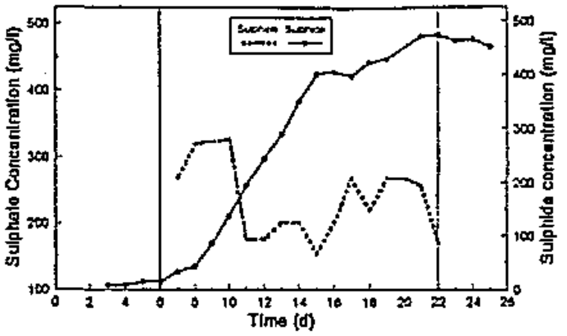


Fig 4.11: Relationship between the sulphide concentrations in the laboratory digester and the sulphate added to the digester.

Sulphide concentrations of greater than 200 mg/l have been shown to be toxic to the methane producing bacteria which results in digester instability and may lead to digester failure (Malina and Pohlan, 1992). While the concentration in the full-scale digester remained below 120 mg/l, concentrations in the laboratory digester rapidly increased to 450 mg/l at which stage methane production had almost ceased and digester failure was noted (Fig 4.12).

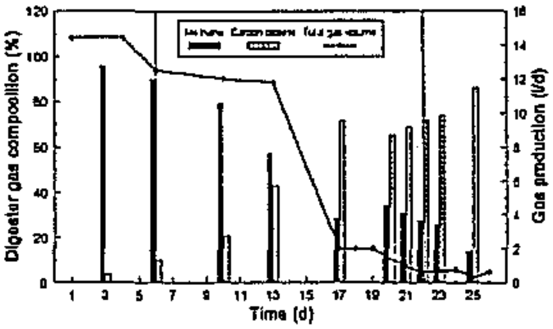


Fig 4.12: Digester gas composition showing a decrease in methane production and concomitant increase in carbon dioxide during co-treatment of reactive dye effluent. The total gas volume measured is shown to decrease over time.

Digester failure occurs as a result of inhibition of the methanogenic bacteria. When this occurs the volatile organic acids (formed in the first stage of the digestion process) are not converted to biogas (methane and carbon dioxide) and instead accumulate in the digester. In a healthy anaerobic digester the volatile acid concentration of the digesting sludge is usually in the range of 50 to 300 mg/l (Ross et al., 1992). These acid concentrations are balanced by alkalinity concentrations in the range of 2 000 to 3 000 mg/l as $CaCO_3$, to give a volatile acid : alkalinity ratio of less than 0.3 (Ross et al., 1992). Thus, the VA:Alk ratio of the digester is a good indication of digester instability, if this rises above 0.3 the process is considered to be unstable.

The volatile acid and alkalinity concentrations in the laboratory digester were stable prior to addition of the reactive dyeing effluent, however, once the co-treatment phase was initiated both the acid and alkalinity concentration of the digester increased rapidly (Fig 4.13). The increase in volatile acids immediately indicated that methanogenesis had been inhibited, however, the concomitant increase in alkalinity meant that the VA:Alk ratio did not indicate digester failure even when methane production had all but ceased. It is not certain what caused the alkalinity of the digester to increase, although it is known that the reduction of sulphate to sulphide generates alkalinity in an anaerobic digester (McCartney and Oleszkiewicz, 1991). With respect to the full-scale trial, the alkalinity of the experimental digester is shown to be consistently higher than that of the control digester, suggesting a similar effect to that in the laboratory digester. However, no marked differences in volatile acid concentration could be seen between the experimental and control digester indicating that the experimental digester was not experiencing methanogenic inhibition (Fig 4.14). The VA:Alk ratios for the experimental and control digesters are stable in comparison to those of the laboratory digester which continued to increase throughout the trial.

Thus, it can be said that the high sulphide concentrations measured in the laboratory digester inhibited the methanogenic bacteria and resulted in digester failure. It must be noted that the VA:Alk ratio is not a suitable analytical tool for detecting digester instability during co-treatment of reactive dyeing effluent due to the increased alkalinity of the digester sludge and it is important that the volatile acid and sulphide concentrations in the digester are monitored closely. The full-scale experimental digester followed similar patterns to the laboratory digester, however, the lower volumes of dye effluent added resulted in lower levels of sulphides being produced which could be tolerated by the methanogenic bacteria.

There are a number of solutions to the problems experienced with sulphate reduction during the anaerobic co-treatment of reactive dye effluent. Firstly, methanogenic populations can be acclimated to tolerate higher levels of sulphides (Isa et al., 1986a; b), and secondly, increasing the labile carbon to sulphate ratio in an anaerobic digester also decreases the inhibitory effect of sulphide reduction. However, sulphides are still undesirable in the anaerobic digestion process due to odour and corrosion problems. One solution is to add a suitable source of heavy metals (such as electroplating effluent) to complex with the sulphides. This approach should be carefully monitored to ensure that the addition is well balanced, as heavy metals are themselves inhibitory to methanogens. In addition, a low concentration of sulphide (1 to 25 mg/l) is required for metabolism of the methanogens. Another option, as sulphate is not thought to be inhibitory to anaerobic digestion, is to control the sulphate reduction process by the addition of molybdate which blocks an initial step in sulphate reduction (Tanaka and Jayadevan, 1994).

A third option would be to change the reactive dyeing recipes to use sodium chloride or sodium carbonate instead of sodium sulphate and recycling the salt using nanofiltration (Erswell et al., 1988), thus removing the problem at source. As a result, the volume of dye concentrate to be transported would be reduced and the salt content of the dyeing effluent would also be substantially decreased, thus decreasing the sodium concentration in the digester.

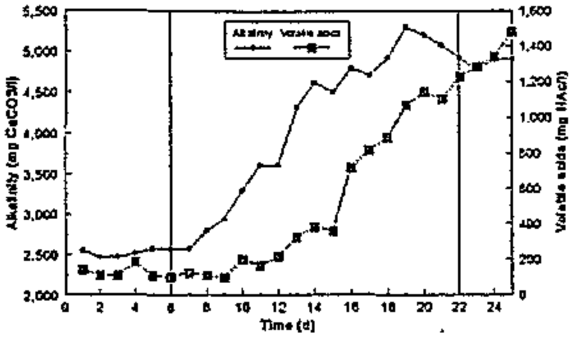
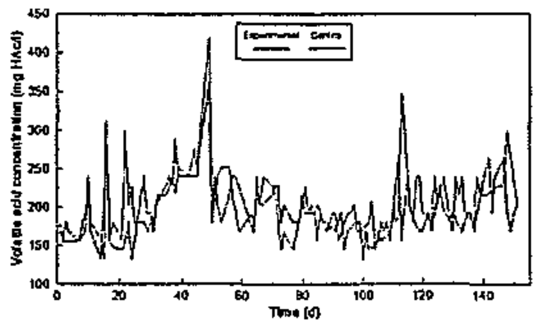
	

Fig 4.13 : The alkalinity and volatile acid concentrations measured in the laboratory digester supernatant before, during and after addition of reactive dye effluent.	Fig 4.14 : Volatile acid concentration for the experimental and control digesters over 151 days.

Annexure 4 contains a number of graphs indicating the stability of the full-scale digester (section 5.1) and the instability and resultant failure of the laboratory digester (section 5.2).

4.7 *Residence Time Distribution Test*

In order to determine the residence time and mixing patterns of the digester used in the full-scale trial, a residence time distribution (RTD) test was performed on digester 2 at the USPW during the co-treatment trial. Details of this test are given in Annexure 10.

A RTD test is carried out by dosing the system with a tracer such as a dye or chemical (of known concentration) and monitoring the output from the system. A knowledge of the flow through the system and the volume are also required. This information is then entered into IMPULSE (Baddock, 1992), a residence time distribution program developed and written by the Pollution Research Group, which will give an indication of the mixing patterns and residence time in the digester.

4.7.1 EXPERIMENTAL

Lithium chloride was chosen as the tracer and tests were carried out on the sludge to ensure that there was no background concentration of Lithium. A solution of Lithium chloride was prepared to give a concentration of approximately 3 mg/l Lithium in the digester and added with the morning feed over 24 min. Samples of the overflow were collected, centrifuged and the supernatant analysed for lithium using an atomic adsorption spectrophotometer (AA) fitted with a lithium lamp. Samples of the feed and the overflow from digester 3 were used as blanks. The instantaneous flow into the digester was calculated from the sludge volumes added to the digesters and the time taken to pump the sludge to the digesters (Annexure 10, Appendix 1). Details of the initial Lithium concentration and the flow at the time of addition, the Lithium concentration in the overflow and the flows to the digester were entered into IMPULSE. It was assumed that the digester was acting as an ideal Mixed Flow Reactor (MFR).

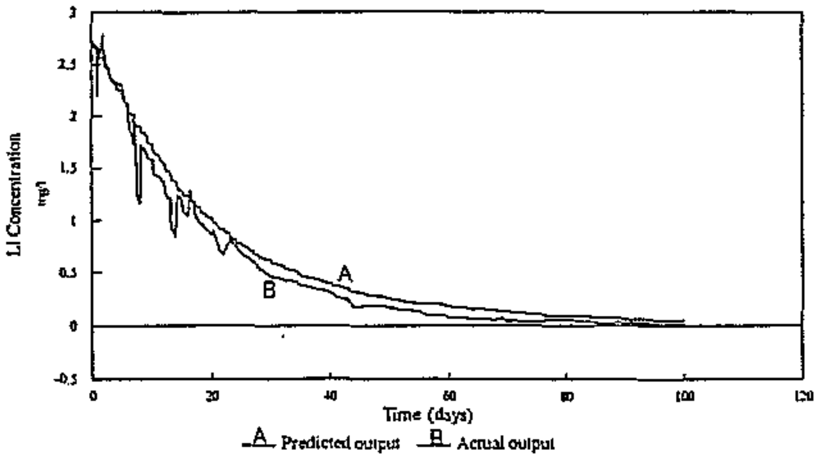


Fig 4.15: Regression of the predicted output and actual output for the Lithium tracer test.

4.7.2 RESULTS AND DISCUSSION

Results of the Li analysis is given in Annexure 10, Appendix 2. From IMPULSE, it was determined that the digester acts as an ideal MFR (see Fig 4.15), but that only half of the actual volume of the digester is active. This implies that the residence time of the digester is only 17.5 d as opposed to 34.5 d. A high recovery of Lithium was calculated (140 %), but this could be attributed to blockages, backflow to the pump sump and unequal distribution of the sludge to the digesters.

It was recommended that RTD tests be performed on the other 3 digesters and that these tests be repeated at 2 yearly intervals.

4.8 Anaerobic Decolourisation of Textile Effluent using a Modified 5-stage Bardenpho Activated Sludge Process

Based on the success of this full-scale trial, experiments are being carried out at the Hammarsdale Wastewater Treatment Plant (HWWTP) to determine the feasibility of using the Bardenpho system to decolourise dyebath effluent. Details of this work is given in Annexure 11. This research project runs in conjunction with the current joint WRC - Umgeni Water - University of Natal project, and is receiving funding from Umgeni Water. It will be completed at the end of 1996.

4.8.1 INTRODUCTION

As mentioned previously (Section 1.6), the final effluent from HWWTW is not complying with standards set by DWAF, especially with respect to chemical oxygen demand (COD), conductivity and colour. Table 4.2 lists the standards for HWWTW effluent and the compliance with these standards for January to May 1994 (Umgeni Water Scientific Services Division,1991). These standards are in the process of being revised.

Table 4.2 : Final effluent standards for Hammarsdale Waste Water Treatment Works and compliance for January to May 1994.

Variable	Unit	Existing Standard	Recommended Limits	Compliance with existing std (%)	Compliance with recommended limits (%)
COD	mg O_2/l	75.0	75.0	81.0	81.0
OA	mg O_2/l	10.0	14.0	56.0	95.0
Conductivity	mS/m	85.0	212.0	0.0	95.0
Colour	°H	0.0	70.0	63.0	63.0
Ammonia	mg/l	10.0	10.0	100.0	100.0
Susp Solids	mg/l	25.0	25.0	100.0	100.0
SRP	µg/l	100.0	1 000.0	81.0	81.0
E. coli	per 100 ml	0.0	50 for 50 % of time and 1000 for 95 % of time	11.0	60 and 84

The following recommendations with regard to the COD, conductivity and colour have been highlighted from this report:

- *Pollution prevention efforts in the Hammarsdale area should continue to be vigorously pursued by Umgeni Water and DWAF to identify and minimise the activities resulting in high oxygen demand of the river upstream from the works*
- *Industries should be encouraged to optimise chemical usage (i.e. reduce the use of* Cl^-, SO_4^{2-} *and* Na^+*) or face increased effluent charges*
- *As a matter of urgency, the wastewater works should investigate costs and methods of reducing colour in the wastewater effluent*
- *Industries should be encouraged to investigate methods of removing colour at source or face increased treatment charges*
- *Umgeni water should support investigations that are currently underway to reduce wastewater effluent colour, such as that currently being pursued by the University of Natal, Pollution Research Group.*

From these recommendations, Umgeni Water and the PRG met to discuss the initiation of this sub-project.

Based on the results of the full-scale trial at USPW, it was proposed that by operating the Bardenpho system at the HWWTW more anaerobically, decolourisation might be achieved. The Bardenpho Process is a 5-stage process where the wastewater is treated in anaerobic, primary anoxic, primary aerobic, secondary anoxic and secondary aerobic zones consecutively to achieve nutrient removal. A detailed discussion of the process is discussed in Annexure 11, Section 4.

4.8.2 EXPERIMENTAL

The research programme was initiated by conducting laboratory experiments to assess the conditions required for anaerobic decolourisation of textile dye effluents and investigating ways of measuring the redox potential of the anaerobic zone at the HWWTW.

A 2 l glass vessel was used as the digester. Mixed liquor (sludge return) from HWWTW was used as the seed sludge and raw sewage was added. The sludge was kept fully mixed at a temperature of 35 °C and the gas production was monitored. A platinum-calomel electrode was inserted into the digester to measure the redox potential along with a temperature probe, both of which were connected to a Copenhagen PHM 95 meter. At a later stage in the experiments a data logging computer was connected to this meter to monitor the redox and temperature at 1.5 h intervals.

In order to determine the redox potential of the anaerobic and anoxic zones in the Bardenpho reactors, samples were collected at various points within the zones and the potential measured.

4.8.3 RESULTS AND DISCUSSION

The initial laboratory-scale experiments showed that the redox potential of sludge from HWWTW lies between -450 mV and -550 mV (SCE). The result of one experiment is shown in Fig 4.16. Since redox potentials are dependent on temperature, the fluctuation in temperature may explain the fluctuations in the redox potential readings.

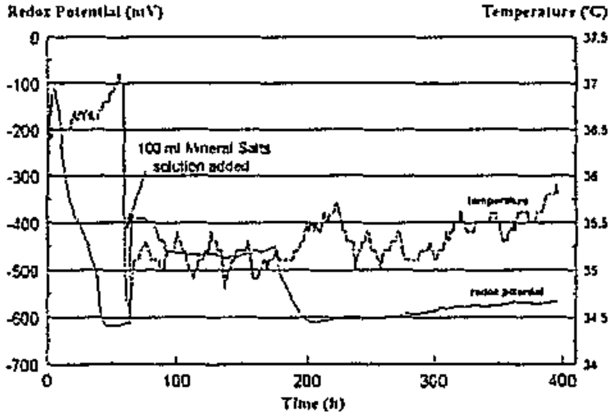


Fig 4.16 : Results of redox potential measurement for 200 ml seed sludge and 800 ml raw swage.

As can be seen, a sharp increase in the redox potential was noticed when the digester was fed with a carbon source (i.e. mineral salts solution which contains vitamins, minerals and glucose). This is due to the readily biodegradable COD fraction being rapidly reduced by the biomass. The plateau from ca. 70 h to ca. 180 h in Fig 4.14 demonstrates when the glucose fraction was being reduced as the redox potential is higher. Based on this observation it can be concluded that addition of a source of COD will result in a rise in redox potential. This analysis will have to be expanded to include simultaneous monitoring of nitrate, COD and colour concentrations in order to determine what components are being reduced and the rate of reduction.

Based on the previous research into the decolourisation of dyes, a potential of less that -250 mV (SCE) is required and that decolourisation was rapid at redox potentials of about - 450 mV (SCE). The laboratory results therefore indicated that decolourisation might be achieved.

The redox potential of the samples taken at the various points in the reactor varied from one point to the next depending on the mixing patterns and the presence of a fatty scum layer, and also from reactor to reactor (**Annexure 11, Section 3.4.3**). It is proposed to construct a redox profile of the anaerobic zone in a reactor in order to determine what conditions are most conducive to low redox potentials. A more effective sampling method is also being developed.

Chapter 5

Chemical Decolourisation

5.1 *The Identification of Dyes and Dye Degradation Products*

5.1.1 BACKGROUND

This study ran in conjunction with the anaerobic decolourisation research. Initially, all investigations were carried out on C.I Reactive Red 141, but were later extended to 3 other dyes; benzeneazo-2-napthol; *p*-sulphpbenzeneazo-2-napthol and C.I. Reactive Red 2. All experiments involved determining the structure of the dye by a number of techniques (e.g. proton and carbon nuclear magnetic resonance spectroscopy (NMR), infrared spectroscopy (IR), ultraviolet spectroscopy (UV), thin layer chromatography (TLC), column chromatography (CC) and high performance liquid chromatography (HPLC)), reducing the dye chemically and biologically and identifying the degradation products.

Details of the experimental work are given in Annexure 2.

5.1.2 CHEMICAL CHARACTERISATION

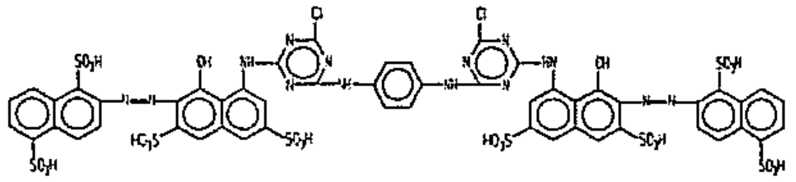
The characteristics of the dyes, such as solubility, purity and structure were determined. The solubility of the dye in various organic solvents was investigated. They were found to be soluble in only polar solvents such as water and methanol. Since C.I. Reactive Red 141 and C.I. Reactive Red 2 are used commercially in the textile industry, they are not pure compounds, but a mixture of different components. Attempts to purify the dyes by column chromatography using silica gel and Amberlite XAD-2 resin were unsuccessful and the use of HPLC was investigated. This was not successful with C.I. Reactive Red 141 as the four peaks identified eluted too close to one another for collection of fractions. However, C.I. Reactive Red 2 was able to be separated and two fractions were collected, one of which was the purified dye. Further experiments were performed on this purified form. Spectroscopic techniques such as NMR, IR and UV were used in the determination of the dye structures.

5.1.3 CHEMICAL REDUCTION

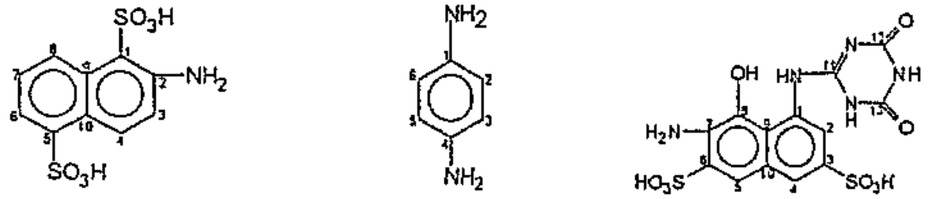
Stannous chloride was found to be the most effective chemical reducing agent. Solutions of the dyes were prepared in methanol and were refluxed with Stannous chloride in hydrochloric acid until decolourised. On cooling, precipitates were formed which were separated and analysed by proton NMR. The remaining solutions were analysed by TLC. By identifying the degradation products, it was evident that in all four cases decolourisation occurred through cleavage of the azo bond.

5.1.4 ANAEROBIC DECOLOURISATION

In order to determine if the same reduction mechanisms were occurring in an anaerobic system, the dyes were subjected to anaerobic digestion. Samples of sludge were obtained from the HWWTW, placed in glass bottles and maintained at constant stirring and temperature. The dyes were added to the sludge (each dye was tested in individual laboratory digesters) and the rate of decolourisation monitored by measuring the absorbance of the samples in the visible region against a blank (sludge). When the absorbance readings of the samples and the blank were the same, digestion was discontinued. The digested samples were evaporated to dryness and the residues analysed. It was found that the same degradation products were formed as for chemical reduction, thus confirming that decolourisation did occur through cleavage of the azo bond. Figs 5.1, 5.2, 5.3 and 5.4 summarise the degradation products identified from chemical and anaerobic degradation of the four azo dyes investigated.

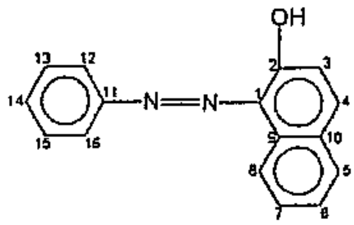


C.I. Reactive Red 141



2-Amino-1,5-naphtholenedisulfonic acid **1,4-Diaminobenzene**

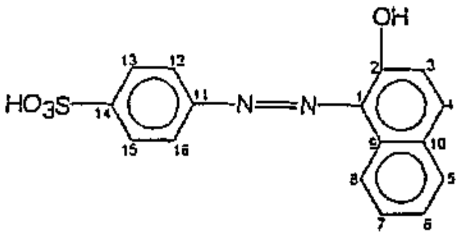
Fig 5.1 : Degradation products of C.I. Reactive Red 141



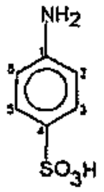
Benzeneazo-2-naphthol

Aniline **1-Amino-2-naphthol**

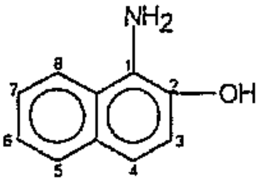
Fig 5.2 : Degradation products of Benzeneazo-2-naphthol



p-Sulpho-benzeneazo-2-naphthol

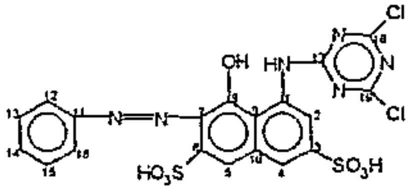


p-Aminobenzenesulphonic acid

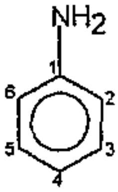


1-Amino-2-naphthol

Fig 5.3 : Degradation products of *p*-Sulpho-benzeneazo-2-naphthol



C.I. Reactive Red 2



Aniline

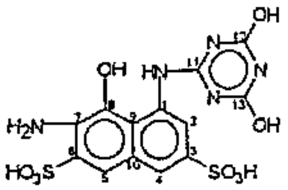


Fig 5.4 : Degradation products of C.I. Reactive Red 2

5.1.5 CHEMICAL OXIDATION

At the beginning of this research project, some experiments were performed to investigate the effect of oxidation processes on solutions of C.I. Reactive Red 141. Methods investigated included the use of hydrogen peroxide, ultraviolet irradiation and Fenton's Reagent. In all cases, decolourisation was observed, but analysis of the resultant precipitates and solutions was difficult. Attention was then turned to the reduction process described in the previous sections and oxidation techniques were not investigated further.

5.2 *The Pinetown Colour Committee*

5.2.1 BACKGROUND

During 1988 and 1990, the Department of Water Affairs and Forestry (DWAF) received a number of complaints concerning colour in the Umbilo River. The origin of the problem was traced back to the discharge point from the USPW. Due to increasing public pressure and stricter DWAF policies, the Borough of Pinetown was requested to implement steps to reduce the colour in the final effluent by May 1991. As a result, the Colour Committee was convened in May 1990 to consider methods of solving the problem of colour in the Umbilo River (Annexure 24). It was comprised of representatives from the local textile industries, the Borough of Pinetown, the University of Natal (through the Pollution Research Group), the Water Research Commission, and was chaired by DWAF. In the first year, invitations were issued to companies to submit proposals to the Borough of Pinetown as to their solution to this problem together with the costs involved. A joint proposal by Explochem Water Treatment and the Pollution Research Group was accepted in October 1990.

Four Pinetown textile industries were involved with the Committee. Factories A and B are the two larger factories and process mostly cellulose-based and polyester fibres. Reactive and disperse dyes are used. Factory C dyes and prints carpet fibres with acid and metal complex dyes, while Factory D dyes lace and lingerie fabrics with acid and disperse dyes. Factory C closed down in June 1992 and Factory B was bought by another textile company in July 1994.

5.2.2 COLOUR GUIDELINES

A colour balance was undertaken over a 14 month period (April 1990 to May 1991) to determine the source of the colour and the degree of colour removal achieved through USPW. A direct correlation was found between the textile industry discharge and the colour in the final effluent from the USPW (see Fig 5.5).

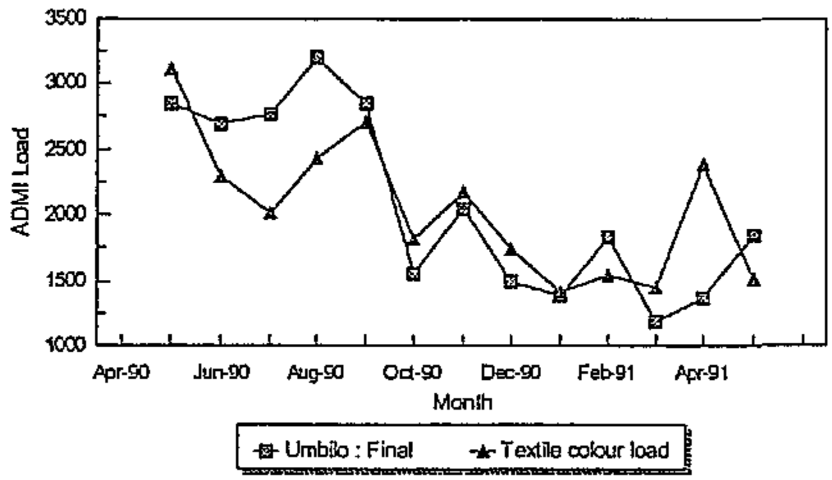


Fig 5.5 : Comparison of total textile effluent colour load and the colour load in the final effluent from the Umbilo Sewage Purification Works.

The estimated colour removal over the USPW was 45 % and the colour in the Umbilo River was increased by approximately 50 % due to the USPW discharge (comparison of colour above and below discharge point). It was decided by the Committee that a guideline value of 500 ADMI units be set as the limit allowed to be discharged to sewer by each textile mill (November 1992). In May 1994, this guideline was reduced to 400 ADMI and DWAF issued a statement that *the final effluent colour (from the Umbilo Sewage Purification Works) should be such that it does not give rise to public complaints and effluent leaving dyehouses should be such that it's contribution to the Umbilo Sewage Purification Works does not cause the colour of the final effluent to be visually displeasing.*

5.2.3 AVAILABLE COLOUR REMOVAL TECHNOLOGIES

Based on a literature survey of available colour removal technologies and a survey of existing treatment plants both nationally and internationally (see Tables 5.1 and 5.2), three methods were chosen for investigation; namely :

- adsorption and coagulation using a cationic electrolyte;
- adsorption and flocculation with ferrous sulphate; and
- oxidation using Fenton's Reagent (ferrous sulphate and hydrogen peroxide).

Tests were performed on concentrated dye liquor from the four factories. In addition, simulated samples of dyehouse fence and sewage effluents were tested and the costs of these operations compared.

The chemical costs for all 3 processes studied were similar for 90 % removal (see Table 5.3). From the results of the tests, it was evident that for Factories A and B either COLFLOC or Fenton's could be used, whereas only fenex was suitable for treating the effluent from Factories C and D.

Table 5.3 : Comparison of treatment costs (1992) for COLFLOC, ferrous sulphate and Fenton's Reagent.

	Cost / kl effluent	Cost / kg fabric	Factory applicability
COLFLOC	R 13.80	14 c	A and B
Ferrous Sulphate	R 11.00	11 c	A, B and D
Fenex	R 10.00	10 c	A, B, C and D

More intensive tests were performed on the effluent from Factory A using COLFLOC and Fenton's Reagent to compare treatment costs and colour removal efficiency (see Annexure 24). Based on the results of this study and the fact that an effective process was required to treat a wide range of dyes, Fenton's Reagent was chosen to be the most suitable process. A pilot-plant was commissioned in March 1993 at a textile mill in the Pinetown area (Factory E).

Table 5.1 : Summary of available textile effluent treatment technologies

Technology	Examples	Advantages	Disadvantages
Coagulation/ flocculation	alum lime iron polyelectrolytes	* simple equipment * relatively rapid colour removal * significant reduction in COD	* large volumes of sludge may be generated * continual addition of chemicals * high running costs * carry-over of polyelectrolytes may affect sewage works
Membranes	reverse osmosis nanofiltration ultrafiltration	* removes impurities of particular molecular masses * good colour removal * fast * can handle large volumes	* high capital costs * some effluent cannot be treated * concentrate contains almost all impurities * concentrate must be treated by another technology prior to disposal * impurities in purified stream may be too high for re-use * regular cleaning is required
	dialysis	* purified stream could be re-used * cation stream could be re-used to regenerate water softener, or as caustic or carbonate in the dyeing process	* portion of the effluent is not treated * concentrate contains almost all impurities * at least one of the concentrates must be treated by another technology * organic material could foul membranes * non-ionic species are not removed * capital and operating costs not known
Adsorbents	activated carbon, silica, charcoal, peat, synthetic polymers etc.	* good colour removal * simple technology * low operating costs for some adsorbents	* high capital cost * slow * can only handle small volumes * regeneration or disposal costs * no single adsorbent is suitable for all dye types * required dosage may be high
Oxidation	Ozone	* good colour removal * can handle large volumes	* High capital costs * high operating costs * not effective at removing colour from all dye types
	Fenton's reagent	* rapid decolourisation * simple operation * sludge enhances sewage works operation	* unknown oxidation products * high running costs
	UV / peroxide UV / catalyst	* good colour removal * powerful oxidant * effective at destroying organic compounds	* high capital costs
	chlorination	* inexpensive * good colour removal	* chlorinated by-products
Reduction	tin chloride hydrosulphite	* good colour removal * effective for decolourising azo dyes	* aromatic amines may be formed * incomplete degradation
Biological	Aerobic	* suitable for removing colour due to insoluble dyes * usually results in mineralisation of dyes	* does not remove colour due to soluble dyes such as reactives * large volumes of sludge are generated * large energy requirements
	Anaerobic	* non-specific colour removal * decolourises most dyes through reduction mechanism * methane produced can be used as energy on-site	* unknown degradation products * high capital cost
Evaporation		* concnetrates effluent stream	* does not "treat" colour
Irrigation		* inexpensive	* detrimental effect on soil * suitable only for uncoloured and non-toxic streams

Table 5.2 : Some operational textile effluent treatment plants					
Location & Date	**Situation**	**Technology**	**Process steps**	**Flow (kl/d)**	**Results**
Germany, 1982	*dye machine*	coagulation (COLFLOC)	*Inject polyelectrolyte into dyebath discharge*	600	* 60 % colour removal * effective for anionic dyes
Germany, 1982	factory discharge	coagulation (COLFLOC)	* inject polyelectrolyte into final effluent * discharge floc to sewage works	2 000	* 70 % colour removal * effective for anionic dyes
Germany, 1982	sewage works	coagulation (cationic poly)	inject polyelectroyte into activated sludge	6 000	* 60 % colour removal
Germany, 1983 Lorrach Wiese Valley	sewage works	biological	* activated sludge * anaerobic digestion of sludge	100 000	
Germany, 1990 Grenzach	factory discharge	membrane (tubular NF)	* direct membrane treatment * salt water recycled * wet air oxidation of concentrate	700	
Japan, 1977 Kyoto	sewage works	biological	activated sludge process	40 000	* poor colour removal
RSA Mooi River Textiles	factory discharge	biological	* aerated lagoon * biofilter * maturation ponds * river	1 000	* COD reduced from 320 to 50 ppm
RSA, 1963 DaGama King Williams Town	factory discharge	land	* land * dairy farming	5 000	
RSA, 1963 DaGama East London	factory discharge	biological	* flocculation * bio-filter * maturation ponds * river	4 500	*effluent complied with general standard
RSA, 1971 Mondi paper	sewage works (textile, domestic)	biological, coagulation, carbon	* activated sludge * alum * granulated activated carbon beds	10 000	* water recycled for paper making
RSA, 1988 HWWTW	sewage works (textile, domestic)	biological	alum added to activated sludge		
RSA, 1989 Dyefin textiles	factory discharge	oxidation (ferrous sulphate)	* addition of ferrous sulphate * addition of caustic * sewer	300	* no colour in sewage works effluent
RSA, 1994 Mym Textiles Umzinto	factory discharge segregated scour rinse and dye streams	membrane	* hyperfiltration * recycle of permeate	200 to 300	* permeate recycled * membrane fouling
RSA, 1995 Ninian & Lester	factory discharge	oxidation (Fenton's reagent)	* effluent segregation * pH reduced to 3 with sulphuric acid * ferrous sulphate addition * hydrogen peroxide addition * lime addition * discharge to sewer	800	* no colour entering sewage works * sludge enhances sewage works operation

Table 5.2 cont. : Some operational textile effluent treatment plants					
Location & Date	**Situation**	**Technology**	**Process steps**	**Flow (kl/d)**	**Results**
RSA, 1993 Dyefin Textiles	factory discharge	oxidation (Fenton's reagent)	• effluent segregation • pH reduced to 3 with sulphuric acid • ferrous sulphate addition • hydrogen peroxide addition • lime addition • discharge to sewer	800	• no colour entering sewage works • sludge enhances sewage works operation
RSA, 1995 Standard Textile	factory discharge	oxidation (Fenton's reagent)	• effluent segregation • pH reduced to 3 with sulphuric acid • ferrous sulphate addition • hydrogen peroxide addition • lime addition • discharge to sewer	800	• no colour entering sewage works • sludge enhances sewage works operation
Sweden, 1976	factory discharge	alum	• addition of alum • flotation • sludge to press	2 880	• reduced COD from 400 to 100 mg/l
Switzerland, 1990	factory discharge	membrane (tubular NF)	• membrane treatment • salt / water recycle	250	
Taiwan, 1990 Far Eastern Textiles	factory discharge	COLFLOC	• equalisation • COLFLOC • alum • flotation • sludge dewater		• good colour removal
Turkey, 1990 Erdogan	factory discharge	biological	• nutrient addition • activated sludge	110	• COD reduced from 1 200 to 600 ppm • produced 0.12 kg/l sludge
Turkey, 1990 Kom	factory discharge	ferrous sulphate, lime	• ferrous sulphate and lime addition • settling • sludge to press	700	• COD reduced from 600 to 360 ppm • produced 2,9 kg/kl sludge
UK, 1978 printing	factory discharge	alum	• alum, lime coagulation • flotation • recycle	2 700	• good colour removal
UK, 1988 carpet weaver	factory discharge	membrane (tubular UF)	• direct membrane treatment • permeate recycled • concentrate to tanker	190	• reported to be successful
USA, 1975 Alabama	factory discharge	oxidation	• electro-coagulation with aluminium • flotation	320	• effluent recycled
USA, 1976 Salem carpet	factory discharge	oxidation (chlorine)		7 200	• treated effluent recycled
USA, 1977 Vernon	sewage works	biological, carbon (PACT)	• carbon addition to aeration tank • wet air regeneration	13 000	• colour removed
USA, 1977		encapsulation of solids	• reaction of metal ions with silicates to form insoluble metal silicates • addition of polymer to form solid gel • waste disposal	1 600 mobile	• heavy metals removed

Table 5.2 cont. : Some operational textile effluent treatment plants

Location & Date	Situation	Technology	Process steps	Flow (kl/d)	Results
USA, 1980 (75% PE, 25% cot)	factory discharge	coagulation, biological	* lime and poly coagulation * aerated lagoon	2 700	* ADMI reduced from 100 to 75
USA, 1980 (80% PE, 20% cot)	factory discharge	biological	extended aeration	3 300	* ADMI reduced from 1300 to 500
USA, 1980 Vernon	sewage works	PACT	* activated sludge * powdered activated carbon with aeration tank * wet air regeneration	24 500	* ADMI reduced from 300 to 30
USA, 1980 (100% PE)	factory discharge	biological, coagulation	* activated sludge * alum and poly coagulation * sludge to centrifuge	2 700	* ADMI reduced from 1340 to 110
USA, 1981 LaFrance	coupled to dye machine wash range	membrane	* hyperfiltration * recycle of permeate	550	
USA, 1981 Penn Dye and Finish Co.	factory discharge	biological	* activated sludge * alum * settling * centrifuge	7 500	* colour reduced by 63 % * BOD reduced by 76 %
USA, 1982 Pennsylvania (bleach wash)	factory discharge	biological	* activated sludge * sludge to anaerobic lagoon	340	* COD reduced from 2 080 to 380 ppm
USA, 1969 Hollitex carpets	factory discharge	adsorption	granulated activated carbon	1 900	* 80 % of effluent recycled
USA, 1989 East Burlingam	sewage works	biological, PACT	* activated sludge * powdered activated carbon with aeration tank * wet air regeneration	45 000	* complete colour removal

Based on the results of the pilot-plant study, it was decided that the fenex process was a suitable technique for removing colour from dyehouse effluents. All Pinetown textile factories were therefore given a deadline to submit proposals to the Borough of Pinetown as to what treatment process would be installed at the respective factories in order that their final effluent complied with the 400 to 500 ADMI limit. It was also agreed by the Committee that any new textile factory opening in Pinetown should be considered a *new player* and be obliged to comply with this effluent discharge standard; i.e. they would have to install a treatment plant prior to commencing operation.

5.2.4 CONCLUSION

The Committee was successful in bringing about co-operation between the textile industry and the local authorities resulting in a commitment on both parts to resolve the problem of removing the colour in the Umbilo River. The studies conducted by Explochem Water Treatment identified 2 suitable techniques for removing colour from textile effluents; i.e. COLFLOC and Fenton's Reagent, and calculated the respective costs of treatment to the factories. Based on in-depth laboratory tests, it was decided that Fenton's Reagent was the more appropriate as it was effective in removing colour from a wide range of dyes, the presence of iron ions was beneficial to the operation of the sewage works, it was simple to operate and had low capital and operating costs. A pilot-plant was established at Factory E in Pinetown and monitored closely over an 8-month period.

Based on the success of the pilot-plant study, similar treatment plants have been installed at Factories A and B. The effect of these plants on the colour in the Umbilo River is difficult to access due to the excessive rainfall received in the months following the commissioning of the plants, but it is felt that they can only result in improvement of the down-stream river colour. Since the pressure on the industries originated from public complaints, it would be pertinent to conduct surveys down-stream from the USPW to determine if the public is aware of any improvements in the appearance of the river.

5.3 Electrochemistry of Dyes

Based on the research into the anaerobic decolourisation of C.I. Reactive Red 141 and the observation that this reaction is dependent on the redox potential of the system, it was thought that if the redox potential of various dyes were known, it would be possible to determine if they would be decolourised anaerobically. The development of a suitable electrochemical procedure would result in a rapid screening test for the susceptibility of compounds to reduction. It would also enable the identification of degradation products. The use of polarography was initially investigated (Annexure 7) but proved unsuccessful. Work is now being done on the use of cyclic voltammetry by Mr Amos Mphephu in the Chemistry Department under the supervision of Prof H Brookes. It is due to be completed in 1996.

5.4 The Identification of Xenobiotic Compounds

In 1992, a study was undertaken by the University of Natal, Umgeni Water and the WRC to analyse for, and identify, xenobiotic components in the HWWTW final effluent. The study was later extended to include the analysis of the influent to the works with the ultimate aim of isolating incoming xenobiotic components and tracing them back to the industry responsible.

A number of compounds were identified in the final and incoming effluent of the HWWTW, a few of which could be traced to two of the textile factories in the surrounding area (Adams, 1992). Of greatest note was the presence of 2-N-octyl-4,5-dihydroisothiazolone in the final and incoming streams and in the effluent from one of the textile mills. This compound is a biocide used in cooling towers to prevent algae and microbial growth. Although it was identified in textile effluent, it could be present in any industry with cooling towers. It has a low probability of degradation, and, based on the calculation of the theoretical COD, was found to have a high potential contributing COD factor

Due to the complex nature of the effluent discharged to HWWTW, it was difficult to develop a single extraction and analytical technique that would detect all xenobiotic compounds. Some of these substances are non-volatile, polar or thermolabile which makes identification by GC-MS difficult.

5.5 Future Research

A project has been initiated with the USPW in Pinetown to investigate the degradation products formed during the Fenex process. As mentioned previously (section 2.2.2), this process involves the use of ferrous sulphate and hydrogen peroxide. The reaction is carried out at pH 3 and involves the oxidation of ferrous ion to ferric ion with the simultaneous production of a hydroxyl radical. This radical is a powerful oxidising agent and will attack the dye compounds and cleave the bonds, thus resulting in decolourisation. As mentioned in Chapter 1, section 1.6, two of the textile industries in the Pinetown area have installed Fenex treatment plants at their factories. While this results in a reduction in the colour discharged from the factories to the USPW, it is not known what compounds are being formed and their toxicity. A student from the USPW, in conjunction with Prof Raynor and Dr Mulholland from the Department of Chemistry and Applied Chemistry at UND, will be investigating this problem. As with the previous laboratory studies, studies will initially concentrate on single azo dyes such as C.I. Reactive Red 141, C.I. Reactive Red 2 and *p*-Sulpho-benzeneazo-2-naphthol.

Chapter 6

Waste Minimisation in the Textile Industry

6.1 Introduction

Waste minimisation is a technique which involves a study of the processes in use at an industry and the identification of areas within the manufacturing processes were savings can be made in terms of water, energy and chemical consumption. This leads to a reduction in both the volume of effluent from the industries as well as the effluent load entering the wastewater treatment works. There are four main steps involved in a waste minimisation survey (Laing, 1991) :

- reduction of pollution at source;
- recycling / reusing waste streams that cannot be avoided;
- treating unavoidable waste streams; and
- ultimate disposal of residual waste.

Waste minimisation action plans would include such actions as :

- identification of all sources of waste;
- quantification of the losses;
- investigation of opportunities to reduce waste;
- setting targets;
- setting priorities; and
- resource allocations.

The first two steps are the most important. Once they have been investigated, priorities can be set based on, for example, environmental impact, regulations, recovery potentials etc.

The identification, characterisation and quantification of waste streams involves the establishment of material balances throughout the various processes in the factory. This involves a study of all the inputs, the process technology and the outputs. For example, on the input side would be substances such as yarn or fabric, dyestuffs, auxiliaries (listed individually), water and energy. On the output side would be the effluent stream containing exhausted dyes and the auxiliaries, the dyed cloth and any gaseous discharges or solid wastes. Non-productive processes such as cleaning of equipment etc. must also be included. Once these have been quantified, the environmental impact can be assessed in terms of COD, BOD pH, toxicity etc.

Once the waste streams have been identified and assessed, the four waste minimisation steps listed above can then be implemented.

6.1.1 REDUCTION AT SOURCE

This involves the elimination or reduction of the pollution potential of a process, the water consumption and the effluent production. This can be achieved in a number of steps :

- optimisation of chemical use and storage;
- changes in process;
- updating equipment;
- improved house-keeping; and
- segregation of waste streams.

Both the suppliers and the manufacturer play a role in this area. Examples include the development of dyes with better exhaustion and fixation, selecting auxiliaries with a high degree of ultimate biodegradability, using newer equipment with lower liquor ratios, computerising dyeing procedures and reducing spillages. Although there may be an initial capital outlay, the pay-back time is relatively short.

6.1.2 RECYCLING AND RE-USE

Reuse involves returning exhausted dyebath liquor and making it up to strength for subsequent dyeing operations. Recycling involves the taking the effluent from one operation and using it elsewhere with or without any treatment, e.g. using the final rinse water from one process as the first rinse water for another.

6.1.3 TREATMENT AND DISPOSAL OF WASTES

Even after effective waste minimisation programmes, there will still be waste that must be treated and disposed of. The treatment route chosen must be one that is suitable for the particular effluents produced. Examples include, separation, neutralisation, chemical treatment and biodegradation.

The main underlying theme of current and emerging legislation is the polluter-pays principle. Therefore, it is essential that industries reduce their environmental impact. Waste minimisation plays an important role in this area and must be viewed as part of the overall business strategy of the textile companies.

6.2 Case Studies

At the outset of this project, it was envisaged that waste minimisation surveys would be conducted at all the textile mills in the Hammarsdale area. This region was chosen due the large number of textile industries in close proximity to one another. However, with the shift of focus onto the Pinetown region, this work was put on hold until 1995. Waste minimisation surveys have been conducted at De Nim (Hammarsdale; 1993), David Whitehead and Sons (Tongaat; 1994 and 1995), Gelvenor (Hammarsdale; 1995) and Natal Threads (Hammarsdale; 1995). The latter two were conducted as part of a joint project with the Environmental Monitoring Group (EMG) in Cape Town and is funded by a Dutch organisation, HIVOS (Humanistische Instituut voor Ontwikkelingssamenwerking). This will be discussed in more detail in Section 6.3.

6.2.1 DE NIM TEXTILES

De Nim Textiles was the first industry approached in Hammarsdale, as the PRG had a good working relationship with the company. Preliminary work involved a study of the processes in use at the factory, the water flow through the factory and the identification of the areas where savings could possibly be implemented. Each machine in the dyehouse was studied individually and an idea obtained of the recipes used, the water consumption and the chemicals discharged to drain. The production data and water consumption for the jiggers were analysed in detail to give an indication of the amount of savings that could be made in monetary terms if certain suggestions were followed, such as the re-use of rinse water and the installation of a heat exchanger. This type of in-depth study was to be performed on all the machines in the dyehouse. The data was compiled into a report, and submitted to De Nim.

6.2.2 DAVID WHITEHEAD AND SONS

A survey was conducted at David Whitehead and Sons over a period of 3 months in 1994 in order to gain background information on the various processes and the type of effluent produced at each stage of the operations. Recommendations were made as to the most suitable effluent treatment options. Based on the results of this survey, ECOSERV (a spin-off consulting firm from the PRG) was awarded a contract at the factory to carry out an in-depth waste minimisation survey and to implement an environmental management system programme at the factory.

6.3 *Environmental Monitoring Group Project*

The Environmental Monitoring Group (EMG) is a non-governmental organisation formed in 1992 from the Centre for Development Studies at the University of the Western Cape. The EMG makes policies, manages projects and does some campaigning. Their ultimate aim is to establish a clean production centre of expertise at EMG. As mentioned previously, a joint project has been undertaken with the EMG. A contract has been signed between the EMG and the University of Natal to undertake the research and a co-operative agreement has been signed between the EMG and the WRC.

6.3.1 BACKGROUND

Industrial development is crucial to the future of South Africa. A Cosatu initiative, the Industrial Strategy Project (ISP), embarked on in 1992, researched broad economic issues relating to the restructuring of South African industry. Considerable emphasis was placed on the growth potential of so-called *dirty* industries (minerals, pulp and paper, textiles and chemicals). With the industrial sector seen as the solution for future growth, there was limited consideration of the environmental consequences of industrial development. Consequently the EMG, a non-governmental organisation based in Cape Town, set up a research programme to run parallel to the ISP, looking at the environmental aspects of the industries which were being investigated. This project is a part of this research programme and will investigate the applicability of cleaner production within the textile industrial sector.

6.3.2 SURVEYS

To date, two surveys have been carried out in detail in the Hammarsdale area; one at Gelvenor (weaving and finishing) and the other at Natal Threads (spinning and finishing of yarns).

Data has been collected from two industries in the area (details are given in Annexure 12) with regard to manufacturing processes, recipes used, water and chemical consumptions and effluent production. Table 6.1 summarises the type of calculations that will be made for each process in order to determine the concentration of dyes and chemicals to drain. Suggestions will be made as to how to reduce the quantity and nature of effluent to drain through waste minimisation (i.e. good house keeping) and recycling. In particular, ways of reducing colour and salt will be investigated.

In addition, information will be collated from the safety data sheets to determine the biodegradability and toxicity of the chemicals discharged to drain and interviews held with the health and environment officers to determine any existing environmental policies of the factory.

It is envisaged that textile industries in other regions of South Africa will be visited and similar surveys conducted to obtain a broad picture of the environmental performance of the South African Textile industry.

This project is due to be completed at the end of 1996.

Table 6.1: Typical calculation of concentration of dye to drain for a jig scour/dye process

Fabric	100 % viscose
Batch size	100 kg
Dye class	Direct
Depth of shade	2 %
Dye fixation	85 %
Liquor ratio	5:1
Number of baths	8.00
Weight of dye applied	100 (fabric weight) x 0.02 (depth of shade) = 2 kg
Weight of unfixed dye	0.15 (% unfixed) x 2 (weight of dye)= 0.3 kg
Total water usage	100 (fabric weight) x 8 (number of baths) x 5 (liquor ratio) = 4000 l
Concentration of dye in effluent	0.3/4000 = 75 mg/l or 0.075 g/l

6.4 Waste Minimisation and Textile Effluent Treatment Guide

The PRG has been awarded a new project from the WRC for 1996 to write a guide enabling the textile industries themselves to conduct waste minimisation surveys and implement cleaner production technologies. At the same time, training courses for the employees will be developed in order to educate them in the aspects of health, safety and the environment. This project has the support of both the Textile Federation and the South African Clothing and Textile Workers Union (SACTWU).

Chapter 7

Conclusions and Recommendations

7.1 Anaerobic Decolourisation

Azo dyes are easily decolourised under anaerobic conditions through reduction of the azo bond and subsequent destruction of the chromophore. An in depth investigation was carried out on C.I. Reactive Red 141. Decolourisation was found to be dependent on the initial dye concentration and the presence of an additional carbon source. While prior exposure of the biomass to the dye did not increase the rate of decolourisation, it did increase the micro-organisms resistance to previously inhibitory concentrations of the dye. The presence of nitrate in the system was found to be inhibitory, with decolourisation only occurring after all nitrate had been reduced. The redox potential of the system was therefore important, with a potential of less than -450 mV (SCE) being conducive to rapid decolourisation. Adsorption did account for some colour removal, but as the dye was subsequently decolourised, no differentiation was made between biological and abiotic decolourisation. The combination of decolourisation with the treatment of organic-rich textile effluents showed promising results for an on-site treatment system. The degradation products of C.I. Reactive Red 141 were identified and found to be consistent with azo bond cleavage. They were not thought to be further degraded under anaerobic conditions. The toxicity of these degradation products is also not known. Experiments to determine the toxicity of C.I. Reactive Red 141 showed that some inhibition did occur at the higher concentrations, but this was overcome by using biomass that had been adapted to the dye.

Investigations into the decolourisation of a range of reactive dyes under anaerobic conditions showed that anthraquinone and phthalocyanine - based dyes are more resistant to degradation, but decolourisation was observed in some cases.

From the full-scale trial at USPW, it is evident that anaerobic digestion is a feasible route for treating reactive dyebath effluent. The full-scale digester was not adversely affected by the addition of the reactive dyebath effluent although increased sodium and sulphide levels were recorded. Failure of the laboratory digester occurred due to inhibition by sulphide, but it must be remembered that this digester was shock-loaded and was not allowed time to acclimate to the dye effluent. It is suggested that if anaerobic systems are to be used as a treatment route for textile effluents, substitutes for sodium sulphate in the dyeing process, such as sodium chloride or sodium carbonate, should be investigated. The other advantage of this replacement would be that the salt streams could be recycled in the factory thus saving water, salt and energy.

The current research work at HWWTP will include laboratory-scale studies into the decolourisation of other classes of dyes (e.g. direct and acid). These dyes are not thought to be a major problem as they have much higher exhaustion rates than reactive dyes and will therefore be present in much lower concentrations in the effluents. In addition, many of them are based on the azo system and should therefore be easily reduced. Once the preliminary redox potential measurements have been completed at the sewage works, full-scale trials will be initiated.

7.2 Chemical Analysis

Chemical reduction of azo dyes results in cleavage of the azo bond to give the corresponding aromatic amines. This mechanism has been shown to be the same as that occurring under anaerobic conditions. The commercially available dye formulations were found to be very impure which resulted in numerous problems in their analysis. HPLC proved to be the most suitable technique for purifying, separating and analysing the dyes and their degradation products.

The use of electrochemical methods for determining the redox potential of various dyes could be a useful tool in determining the susceptibility of these dyes to decolourisation under anaerobic conditions. However, the impurity of the available formulations has caused a number of problems in this investigation.

Further research is also required into identifying the degradation products formed during oxidative processes. This is currently under investigation in a joint project with the USPW and the Department of Chemistry and Applied Chemistry.

7.3 Waste Minimisation

Before an industry considers the installation of an effluent treatment plant, a waste minimisation survey should be conducted at the factory. This is a four step process involving reducing pollution at source; recycling or reusing waste streams; treating unavoidable wastes and disposing of residual wastes. In this way, water, chemicals and energy are saved and there is less effluent that needs treatment and disposal.

Currently, surveys are being conducted at two textile industries in the Hammarsdale region, but it is hoped to extend this study to include a range of textile industries throughout South Africa.

7.4 Recommendations

- Reactive dye concentrates can be treated in a conventional anaerobic digester;
- The combination of an anaerobic-aerobic treatment system should be investigated;
- Further research into the co-treatment of dye concentrates and the high COD streams such as scouring and desizing effluents should be conducted;
- The toxicity of dye degradation products need to be determined;
- A waste minimisation guide should be prepared for the textile industry;
- Factories should investigate implementing waste minimisation, effluent recycling and pollution prevention .

Further research is being conducted at the HWWTW into the feasibility of using a dedicated Bardenpho reactor to treat dye concentrates. Waste minimisation surveys are currently being conducted at textile industries in the Hammarsdale area as part of a joint project with the EMG. As both these project are only due to be completed at the end of 1996, it is recommended that some provision be made to include the completed reports with this project.

Chapter 8

Technology Transfer

8.1 Interaction With Other Projects

The residence time distribution test carried out on the digester used in the full-scale trials at USPW was interpreted using IMPULSE, which was developed during the course of WRC project No. 363 entitled *The Development and Evaluation of Small-scale Potable Water Treatment Equipment.*

8.2 Ad Hoc Assistance

During the course of the project, ad-hoc assistance has been given to:

- Pinetown Colour Committee
- Durban Corporation
- Pinetown Municipality
- Ninian and Lester Pty (Ltd)
- David Whitehead and Sons
- Explochem
- ECOSERV
- Department of Water Affairs and Forestry

The PRG has also been approached by the Lesotho National Development Corporation to assist them in developing a strategy for treating textile effluents. The request was motivated by official approaches by the South African Government to the Lesotho Government about the deteriorating water quality in the Caledon River and its effect on the South African users.

8.3 Publications

8.3.1 PAPERS AND SEMINARS PRESENTED

C.M. Carliell, *The South African Textile Industry : Anaerobic Digestion for Colour Removal,* Water Institute of Southern Africa (Natal Branch), Pinetown, 19 October 1994.

S.J. Barclay, *Minimising Textile Effluent at Hammarsdale,* Ntshongweni Catchment Programme Technical Planning Workshop, Inchanga, 29 November 1994.

S.J. Barclay, *Anaerobic Treatment of Textile Effluent,* International Course: Biochemical Engineering Applications in Environmental Biotechnology and Cleaner Production, Guatemala, 18-29 September 1995.

S.J. Barclay, C.M. Carliell and C.A. Buckley, *Treatment of Exhaust Reactive Dyebath Effluent using Anaerobic Digestion*, WISA '96, Water Institute of Southern Africa conference, Port Elizabeth, 20-23 May 1996.

8.3.2 POSTER PRESENTATIONS

C.M. Carliell, C.A. Buckley and E. Senior, *The Microbial Transformation of Azo Dyes*, Biotech SA '93, First South African Biotechnology Conference, Grahamstown, 31 January to 3 February 1993 (**Annexure 19**).

S.J. Godefroy, C.M. Carliell, N. Naidoo, B.S. Martincigh, D. Mulholland, C.A. Buckley and E. Senior, *Regional Treatment of Textile Effluent*, Water Institute of Southern Africa, Durban, 24 to 27 May 1993 (**Annexure 20**).

C. M. Carliell, S. J. Barclay, N. Naidoo, E. Senior and C. A. Buckley, *Anaerobic Decolourisation of Azo Dyes*, Seventh International Symposium on Anaerobic Digestion, Cape Town, 23 to 27 January 1994 (**Annexure 21**).

D.A. Mulholland and N. Naidoo: *The Identification of Dyes and Dye Degradation Products*, South African Chemical Society, Frank Warren Conference, Avontura-Aldam, Free State, 2-7 April 1995 (**Annexure 22**).

N. Naidoo, D.A. Mulholland, S.J. Barclay and C.A. Buckley: *The Identification, Separation and Degradation of an Azo Reactive Dye (C.I. Reactive Red 2)*, Organic Heterocyclic Chemistry Conference, University of Hong Kong, 13 to 16 August 1995 (**Annexure 23**).

C.B. Bell, S.J. Barclay and C.A. Buckley, *Decolourisation of Textile Effluent using a Modified Bardenpho Nutrient Removal System*, WISA '96, Water Institute of Southern Africa conference, Port Elizabeth, 20-23 May 1996.

C.M. Gilfillan, S.J. Barclay, S. Law and C.A. Buckley, *An Assessment of the Environmental Performance of the Textile Industry in South Africa*, WISA '96, Water Institute of Southern Africa conference, Port Elizabeth, 20-23 May 1996.

8.3.3 PAPERS PUBLISHED IN JOURNALS

C.M. Carliell, S.J. Barclay, N. Naidoo, C.A. Buckley, D.A. Mulholland and E. Senior (1994) *Anaerobic Decolourisation of Reactive Dyes in Conventional Sewage Treatment Processes*, Water SA 20 (4) : 341-344. (**Annexure 13**)

C.M. Carliell, S.J. Barclay, N. Naidoo, C.A. Buckley, D.A. Mulholland and E. Senior (1995) *Microbial Decolourisation of a Reactive Azo Dye Under Anaerobic Conditions*, Water SA 21 (1) : 61-69 (**Annexure 14**)

The following paper has been accepted for publication in Water SA:

C.M. Carliell, S.J. Barclay and C.A. Buckley: *Treatment of Exhausted Reactive Dyebath Effluent Using Anaerobic Digestion: Laboratory and Full-scale Trials.* This paper covers the work that was performed at the Umbilo Sewage Purification Works in Pinetown (Annexure 15)

The following paper has been submitted for publication to Water SA:

N. Naidoo, D.A. Mulholland, C.M. Carliell, S.J. Barclay, C.A. Buckley: *Chemical and Anaerobic Decolourisation of C.I. Reactive Red 2.* (Annexure 16)

8.3.4 THESES

C.M. Carleill, *Biological Degradation of Azo Dyes in an Anaerobic System*, MScEng Thesis, University of Natal, Durban, South Africa , 1993 (Annexure 1)

N. Naidoo, *The Identification of Dyes and Dye Degradation Products*, MSc Thesis, University of Natal, Durban, South Africa, 1994 (Annexure 2)

8.4 Other

Prof. Chris Buckley and Cynthia Carliell visited the United Kingdom from 20 March to 10 April 1994. During this time, a number of wastewater treatment plants were toured and information gained as to the teratment processes in use and their efficiency. A full report is given in Annexure 17.

Dr Dulcie Mulholland spent 6 months in the United Sates on Sabbatical from June 1993 to January 1994. During this time, she visited the Georgia Institute of Technology, a leader in the research of the treatment of textile wastes. Information was obtained on techniques for determining dye purity and analysing degradation products. A detailed report is given in Annexure 18

Tours were also made of various waste water treatment plants in Italy and this has led to possible co-operative research projects being discussed with Prof. Alberto Rozzi from the Politecnico di Milano.

Based on the waste minimisation studies carried out during the course of this project, it became evident that there was a need for a user-friendly guide that would enable the textile industries to conduct their own waste minimisation surveys. A 2-year WRC-sponsored project has therefore been initiated to design such a guide. At the same time, training courses will be developed in order to educate the employees in aspects of health, safety and the environment. This project has the support of both the Textile Federation and the South African Clothing and Textile Workers Union (SACTWU).

8.10 Archiving of Data

The data from this project are presented in Annexures 1 to 27 which are available from the Water Research Commission on request.

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