COLOUR REDUCTION FROM TEXTILE EFFLUENT

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ABSTRACT

The removal of colour from a textile effluent was investigated. Three treatment processes, namely coagulation, chemical oxidation and biological treatment were evaluated.

A combination of ferric chloride with polyacrylamide removed colour by 70 to 80 percent and COD by 30 to 40 percent, respectively. The use of the polyacrylamide as a floc aid improved the floc size and reduced the sludge volume.

In a comparison between ozone, peroxone, hydrogen peroxide and chlorine it was found that ozone at a dose of 30 mg/l removed approximately 48 percent of residual colour. No advantage was found to be gained in using peroxone. A change in hue was observed which was ascribed to changes in absorbances in the visible spectrum.

Activated sludge tests showed that effluent treated by coagulation and ozonation had the greatest biodegradability followed by coagulated effluent and raw effluent. Raw effluent showed some inhibition towards activated sludge. Although activated sludge removed approximately 55% of the colour from the raw effluent, no additional colour removal occurred with the pre-treated effluent. COD removal was excellent in all cases ranging from 55% for the pre-treated samples to 77% for the raw effluent.

The conclusion is drawn that pre-treatment of textile effluent is economically justifiable.

Keywords: Textile effluent, pre-treatment, colour removal, COD removal, coagulation, oxidation, biological treatment.

UITTTREKSEL

Die verwydering van kleurstowwe uit 'n tekstiel uitvloeisel is ondersoek. Drie behandelingsprosesse, naamlik koagulasie, chemiese oksidasie en biologiese behandeling is geëvalueer.

'n Kombinasie van ferrichloried en poliakrielamied as koagulant verwyder tussen 70 en 80 persent van die kleur en tussen 30 en 40 persent van die CSB onderskeidelik. Die gebruik van poliakrielamied as flokkuleerhulpmiddel verbeter die vlokgrootte en verminder die slyk volume.

In 'n vergelyking tussen osoon, perosoon en chloor is gevind dat osoon teen 'n dosis van 30 mg/l ongeveer 48 persent van die oorblywende kleur na koagulasie verwyder het. Hierteenoor het perosoon en chloor geen noemenswaardige effek op kleurverwydering getoon nie. Met alle oksidante is 'n verandering in die tint waargeneem.

Rou tekstiel uitvloeisel toon tekens van groei-inhibisie in geaktiveerde slyk. Hoewel geaktiveerde slyk op sy eie tot 55 persent van die rou uitvloeisel se kleur verwyder, is geen addisionele kleurverwydering vanaf die vooraf gekoaguleerde en geosoneerde uitvloeisel waargeneem nie. Hierteenoor het die geaktiveerde slyk 77 persent van die rou uitvloeisel en 55 persent van die voorafbehandelde uitvloeisel se CSB onderskeidelik verwyder.

Die gevolgtrekking word gemaak dat die voorafbehandeling van tekstieluitvloeisel ekonomies regverdigbaar is.

Sleutelwoorde: Tekstiel uitvloeisel, voorafbehandeling, kleur verwydering, CSB verwydering, koagulasie, oksidasie, biologiese behandeling, kleurstowwe.

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CHAPTER 1 : INTRODUCTION

The wastewater works, which is situated in the Hammarsdale industrial complex between Durban and Pietermaritzburg in Kwazulu-Natal, receives about 70% of its inflow from the textile industries established in the area under an industrial decentralisation plan. Due to the nature of the textile industry, the effluents are highly coloured, resulting in the works receiving a highly coloured influent even after dilution with abattoir and domestic sewage. Details of the quality of the influent and effluent are given in Appendix 1.

Treatment at the works consists of coarse and fine screening followed by an extended aeration activated sludge plant with six parallel 5-stage Bardenpho Reactors arranged radially about a center clarifier. The works has a design capacity of 27Ml/d, but currently operates at 12Ml/d, with a sludge age of 30 days. Alum is added to the anaerobic reactor (120mg/l) to reduce phosphate, colour and chemical oxygen demand. The alum addition also improves settling and clarification which are problematic due to poor floc formation.

After clarification, the effluent is once again treated with alum (80mg/l) in a compartment at the beginning of the maturation river (retention time of 3 days), to further reduce the colour and chemical oxygen demand in order to comply with the General Standard.

The effluent is chlorinated half way through the maturation river and the final effluent is discharged into the Sterkspruit River which flows into the Shongweni Resource Reserve.

Despite the treatment with alum described above, the colour in the final effluent remains too high and previous research has been conducted into removing the residual colour in the effluent from the activated sludge plant. This has included the use of ozone, and the substitution of ferric chloride for alum in the chemical dosing at the beginning of the maturation river (Gaydon and de Haas, 1998).

The focus of this research is the pre-treatment of the textile effluent before discharging it to sewer. This will reduce the dye input to the works and is preferable in that it promotes better management of the effluent stream from the point of generation. It should also prove to be cheaper in that the volumes to be treated will be smaller and the treatment can be tailored to the effluent produced at each specific factory.

The effluent chosen for use in this research is one of the most severely polluted in the area, coming from a major contributory textile mill which produces dyed polyester cotton and polyester viscose fabric from raw fiber, using both reactive and disperse dyes in the dyeing process. These are some of the more difficult dyes to treat.

The investigation was divided into three phases:

- Primary treatment in which the effluent was coagulated and flocculated to remove the majority of the colour and Chemical Oxygen Demand (COD).
- Secondary treatment in which chemical oxidation was used to oxidise the chromophores in the dyes remaining after the primary treatment.
- Tertiary treatment in which the treatability of the pre-treated effluent by activated sludge was assessed in terms of colour and COD removal, and biological inhibition.

CHAPTER 2 : LITERATURE SURVEY

2.1. RESEARCH PROBLEM

2.1.1. TEXTILE EFFLUENT COMPOSITION

Dyehouse effluents are generally highly coloured, and high in temperature, chemical oxygen demand (COD), total dissolved solids, and at times, highly alkaline. Because of the variety of processing systems used, the wastewaters vary both in strength and flow (Treffry-Goatley *et al*, 1991). The treatment of dyehouse effluent is complicated by the number of dyes and other chemicals present in the effluent, and the potential these chemicals have to interfere with any treatment process selected (Judkin, 1981). Large dosages of coagulant, usually alum or lime, are often needed because of the strength of colour and effect of dispersing agents in the waste that may be difficult to overcome (Shelley *et al*, 1976).

In order to understand the nature, variability and complexity of textile effluents, it is necessary to understand the basics of dye and fibre chemistry and textile processing methods. Through an understanding of dye chemistry, a fundamental approach to removing textile colour from effluent streams can be obtained.

A wide variety of chemicals can be found in textile effluent at any time. A list of those commonly found is shown in Table 2.1.

The dye molecule can be considered to be constructed from two components, the dye chromophore and the dye functional group. The dye chromophore portion of the molecule includes double bonds and is responsible for the colour of the dye. When the molecule is exposed to light the structure of the chromophore oscillates, light is absorbed and colour is visible.

Table 2.1 : Chemicals found in textile effluents (Treffry-Goatley *et al*, 1991).

Description	**Composition**	**Function**
Salts	Sodium chloride Sodium sulphate	Displace dye from liquid to fibre
Acids	Acetic acid Sulphuric acid	pH control
Bases	Sodium hydroxide Sodium carbonate	pH control
Buffers	Phosphate	pH control
Sequestering agents	EDTA	Complex hardness Regulate dye application to fibre (retarders)
Dispersing and surface active agents	Anionic Cationic Non-ionic	Disperse dyes Regulate dye application Soften fibre
Oxidising agents	Hydrogen peroxide	Precipitate dyes Bleaching of fibre
Reducing agents	Sodium dithionate	Solubilise vat and sulphur dyes Remove untreated dye after dyeing
Heavy metals	Copper, chrome, cobalt	Improve adhesion of dye to fibre
Spinning oils	-	Aid spinning process
Cotton waxes	-	Naturally occurring
Dyes	Various	Colour fibre
Fibre	Various	Fabric, fibre break - down

There are about twelve chemical classes of chromophore groups and these include the azo, anthraquinone, benzodifuranone, indigo and sulphur groups. The dye functional group is the portion of the molecule that is responsible for the bond between the fibre and the dye. The structure usually includes a benzene ring with an attached reactive group (for example $-SO_3^-Na^+$). The dye is bonded to the fibre, through a reaction between the fibre and the dye functional group, by means of covalent or ionic bonds, van der Waal's forces, or through impregnation of a colloidal dye particle into the fibre (Treffry-Goatley *et al*, 1991).

Table 2.2 classifies ten of the most frequently used dye classes in terms of their method of application to the fibre types. The table also lists the attachment mechanisms, the method of application and the chemicals used. The dye characteristics which are important in selecting a colour removal technology are also provided.

Azo dyes account for 60 to 70% of all textile dyestuffs produced and are the most common chromophore of reactive textile dyes. Colouration of textile effluents (in particular red hues) can usually be linked to the presence of water-soluble (reactive) azo dyes in the wastewater. Generally, azo dyes contain between one and four azo linkages (-N=N-), linking phenyl and naphthyl radicals that are usually substituted with some combination of functional groups including: amino, chloro, hydroxy, methyl, nitro and the sodium salt of sulfonic acid. Azo dyes are of concern because some of the dyes, dye precursors, or their degradation products such as aromatic amines (which are also dye precursors) have been shown to be, or are suspected to be, carcinogenic (Shaul *et al*, 1985).

Natural and synthetic fibres and mixtures of both are processed simultaneously in a dyehouse. Each fibre type has a particular chemical composition and advantage is taken of this to attach the dye molecule to the fibre. More than one dye class can be used with a particular fibre. Each dye class, however, requires a particular physical and chemical environment to promote optimum dye adhesion to the fibre. It thus follows that each particular fibre type with each particular dye produces a particular effluent. This results in widely ranging effluent compositions.

It is evident that due to the variability and complexity of the composition of the textile effluents, it is necessary to assess the techniques and processes used within the textile mill before embarking on a pre-treatment strategy.

Table 2.2 : Dye Classification (Treffry-Goatley *et al*, 1991).

Dye class	**Characteristics**	**Typical assorted fibre**	**Dye-fibre attachment mechanism**	**Typical method of application**
Acid	Anionic Highly water soluble Poor wet fastness	Nylon, wool	Ionic bond	Fibre placed in acidified aqueous media pH 3-5 Fibre assumes a positive charge - dye added and temperature raised to 50-110°C
Metal complex acid dye (dye molecule is complexed with chromium, cobalt)	Anionic Low water solubility Good wet fastness	Nylon, wool	Ionic bond	As with acid dyes pH 5-7
Direct	Anionic Highly water soluble Poor wet fastness	Cotton, viscose	Ionic bond	Fibre placed in slightly alkaline dyebath - add dye and electrolyte (NaCl, Na_2SO_4) to displace dye to fibre, temperature raised to 98°C
Basic or cationic	Cationic Highly water soluble	Acrylics	Ionic bond	Fibre placed in acidified aqueous dyebath at pH 4 - 6 - dye added - temperature increased to 100 to 105°C, dye diffuses into fibre
Dispersed	Colloidal dispersion Very low water solubility Good wet fastness	Polyester, nylon, acrylic, cellulose acetate	Colloidal impregnation, adsorption	Fibre placed in acidified dyebaths pH 4,5 - dye added and temperature raised to 130 °C - causes dye migration into fibre
Reactive	Anionic highly water soluble	Cotton, viscose, wool	Covalent bonds	Fibre placed in aqueous dye solution - add salt to displace dye to fibre. Add alkali to cause reaction between dye and fibre
Sulphur	Colloidal after reaction in fibre Insoluble Wet fast	Cotton, viscose	Dye precipitated *in-situ* in fibre	Fibre placed in dyebath - dye dissolved in alkaline sodium sulphate. Dye displaced to fibre with electrolyte. Dye precipitated *in-situ* with air or peroxide
Vat	As per sulphur dye	Cotton, viscose	Dye precipitated *in-situ* in fibre	As per sulphur dye
Azoic	As per sulphur dye	Cotton, viscose	Dye precipitated *in-situ* in fibre	Fibre placed in dyebath coupler applied to fibre dye chromophore added boiled to precipitate
Mordant or chrome	Anionic water soluble good wet fastness	Wool	Fibre - chrome - dye complex	Fibre placed in acidified dyebath - add sodium dichromate - add dye with temperature at 98 °C

2.1.2. COLOUR IDENTIFICATION AND MEASUREMENT

Accurate colour measurements of raw and treated wastewater are necessary to evaluate the various treatment processes. Colour and its removal are measured using various techniques:

- the ADMI Tristimulus Filter method devised by the now defunct American Dye Manufacturers Institute
- absorbance at a peak wavelength
- absorbance at 400nm ie degrees Hazen
- advanced chromatographic methods.

ADMI Method

The ADMI test is undertaken over the full range of the visible spectrum. It is considered to be more representative of the effluent colour intensity than is the Hazen test which is only performed at a single wave length of 400nm (Treffry-Goatley *et al*, 1991). The ADMI Tristimulus Filter method quantifies hue, intensity, luminosity and purity, and generates a single value for measuring colour relative to a colourless standard (Tozer, 1994).

Absorbance at a peak wavelength

In this method the wavelength of maximum absorbance for raw, filtered wastewater is identified. The dyes absorb this wavelength of light, providing absorbance values that are roughly proportional to the dye concentrations. This technique provides a rough measurement of colour and removal, but it depends on the raw and treated waters having similar hues. It lacks the complexity needed to describe other properties of colour that are independent of hue, such as intensity, luminosity and purity (Tozer, 1994).

Absorbance at 400nm ie degrees Hazen

This is a single wavelength spectrophotometric method (at 400nm) based on potassium hexachloroplatinate standards (204A, Standard Methods, 1985) where 1 degree Hazen (°H) is equivalent to 1mgPt/l of the chloroplatinate ion. This method is used by Umgeni Water for measuring colour in all types of water and, although it lacks the sophistication of the ADMI method, it is simple and affordable.

Advanced chromatographic methods

These include thin layer chromatography (TLC), high pressure liquid chromatography (HPLC), capillary electrophoresis (CE), adsorptive stripping voltammetry (AdSV), gas chromatography (GC), gas chromatography/mass spectrometry (GC/MS), a combination of liquid chromatography with MS (LC/MS).

The problems experienced with these methods are as follows:

- They tend to be specific to a particular dye and its derivatives, but do not extend to mixed effluents. Problems are also experienced in the concentration steps due to the water solubility of reactive dyes adversely affecting organic solvent extraction techniques (Schramm *et al*, 1988).
- Problems in resolving the individual dyes using HPLC and capillary electrophoresis, and a great number of naturally occurring and industrial compounds which also absorb in the UV-Vis region (Croft and Lewis, 1992; Oxspring *et al*, 1995).
- Thermal instability and nonvolatility in gas chromatography/mass spectrometry (GC/MS) (Lin and Voyksner, 1993).
- TLC, although cheap, is time-consuming and not quantitative (Croft and Hinks, 1992).

Although the ADMI method is the most comprehensive method for measuring the perception of colour by humans it requires a complex and expensive dual path spectrophotometer. The measurement of absorbance at the peak absorbance wavelength can only really be applied to effluents containing a limited number of dyes which will then produce such peaks. Complex mixtures of dyes do not produce marked peaks. Oxidation of the effluent can also produce a change in the peak wavelength. The use of advanced chromatographic methods is very complicated and expensive, and is usually limited to simple dye solutions. Good success has not been achieved with "real" textile effluents (Schramm *et al*, 1988).

For the purposes of this investigation colour was measured in degrees Hazen as this was the established method for effluents and comparisons could thus be facilitated. It is also the most commonly used colour measurement method in South Africa, with the ADMI method being infrequently used.

2.2. ENVIRONMENTAL EFFECTS

From a viewpoint of aesthetics, colour is one of the first parameters considered in the field of pollution prevention (Tunay *et al*, 1996). The dyestuffs also absorb light, so the presence of colour may also reduce penetration of light into the water, which can be detrimental to aquatic life, especially where photosynthesis takes place.

Very little is known of the environmental occurrence, toxicity, persistence and fate of dyes, due to difficulties in the determination of different chemical classes of dyes at trace levels in environmental samples (Maguire, 1992).

2.2.1. TOXICITY

The USEPA's Office of Toxic Substances is concerned about effluent discharges because some of the dyes, dye precursors and/or their degradation products such as aromatic amines, are either confirmed or suspected, carcinogens. There is particular concern with regard to the heavily used disperse azo dyes in aquatic environments. The hazard may be compounded for organisms which accumulate these strongly lipophilic disperse dyes and which metabolize them through cleavage of the azo bond, producing the toxic aromatic amines (Maguire, 1992).

As part of an on-going programme designed to investigate the environmental fate and effects of dyestuffs, the Ecological Committee of ETAD (Ecological and Toxicological Association of the Dyes and Organic Pigments Manufacturers) carried out a joint programme of work designed to develop a base set of environmental data on a substantial number of dyes for which the chemical structures are published in the Colour Index.

A total of 47 dyes were tested in the programme and in terms of dye class these consisted of 11 Acid, 11 Disperse, 8 Reactive, 7 Direct, 6 Basic, 3 Mordant and 1 Sulphur Dye. The studies carried out on each dyestuff were a 96 hour acute fish toxicity using the Zebra fish (*Brachydanio rerio*), a 48 hour acute study on *Daphnia magna*, a 72 hour growth inhibition on the alga *Scenedesmus subspicatus*, a bacterial toxicity test using the inhibition of the respiration rate of activated sludge obtained from a sewage treatment works as an indicator of toxicity, and a study based on the OECD (Organisation for Economic Development and Co-operation) test guideline 302B designed to assess the potential for removal of the dyestuff during biological treatment.

The maximum concentration selected for the toxicity tests was 100 mg/l, except for the studies carried out on the alga where a maximum test concentration of 10 mg/l was used due to strong light absorbance. The concentration of activated sludge solids used was 1g/l. This ratio of dyestuff to sludge solids is very much higher than is likely in practice where dyestuff concentrations in textile mill effluents for biological treatment are usually less than 10 mg/l and the activated sludge solids are typically in the range 3-5g/l.

In summary the toxicity results show the following:

- With the exception of the basic dyes, the dyes had little or no effect on the respiration rate of the activated sludge at the limit test concentration of 100 mg/l.

- In agreement with previously reported data most dyes (34 out of 47) have fish LC_{50}[1] values in excess of 100mg/l. The basic dyes were the principle exception to this with all three of the dyes tested having LC_{50} values between 1 and 10mg/l. Of the other seven dyes showing fish 96 hr LC_{50} values below 100mg/l, two dyes were in the range 1-10 mg/l and five dyes in the range 10-100mg/l.
- The *Daphnia magna* results were broadly similar to those found for the fish except that five of the six basic dyes tested showed 48 hr EC_{50}[2] values below 1mg/l.
- The algal data, again, showed that basis dyes are toxic with all six tested having a 72 hr EC_{50} below 10mg/l and two of the six below 1mg/l. However a larger number of other dyes also gave a 72 hr EC_{50} value below the 10mg/l selected concentration limit. It appears from the non-basic dye results that it may be the less soluble substances which have a particular effect on algae and there is possibly also some correlation with colour (Brown, 1992).

No systematic long-term studies on possible sublethal chronic effects of dyestuffs on fish appear to have been reported. Bioaccumulation confirmed that water-soluble dyestuffs do not bioaccumulate. Low bioaccumulation factors were also reported for 12 disperse dyestuffs and these materials are essentially water-insoluble and have a relatively high octanol-water partition co-efficient. This may be as the result of a molecular size limitation which effectively prevents permeation through biological membranes, or the relatively low solubility level of pigments in fat which effectively limits the amount of uptake (Brown and Anliker, 1988).

From the above it is evident that although the textile dyes are not acutely toxic and would not appear to bioaccumulate there is some concern that some of the dyes, their precursors and degradation products, may be carcinogenic.

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[1] LC_{50} - the concentration of toxin in water which causes mortality to 50% of the test population at a stated exposure period.
[2] EC_{50} - the concentration of toxin in water that causes a measurable negative effect on 50% of the test population at a defined exposure period.

The high COD of dyehouse wastes also represents a problem in the aquatic environment, although biological treatment carried out at the wastewater treatment works usually results in acceptable discharges.

2.2.2. PERSISTENCE

Dyes are generally recalcitrant to biodegradation since one of the important factors in selecting a dye is its resistance to oxidation since necessary criteria for their successful use are "light-fastness" and "wash-fastness". Although aerobic biodegradation may not be likely, some researchers have shown azo dyes to be slowly biodegraded under anaerobic conditions (Carliell *et al*, 1995).

An unidentified purple dye obtained from a pollution incident at Saint-Hyacinthe was characterised for its persistence and found to be stable toward sunlight photolysis for at least three years, resisted biological degradation in water-sediment suspensions under aerobic conditions for at least two years, and anaerobic conditions for at least three months (Maguire, 1992).

Dyes, by their very nature, are not readily biodegradable under aerobic conditions, although they are slowly biodegradable under fully anaerobic conditions. In the natural aquatic environment their persistence is of concern.

2.2.3. FATE

As part of a study that the United States Environmental Protection Agency (EPA) undertook, entitled Fate of Water Soluble Azo Dyes in the Activated Sludge Process, Shaul *et al*. (1991) 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 weight of the dye also seemed to influence the reactivity as the compounds that were adsorbed had higher molecular weights. It was suggested that sulphonation was a major factor in preventing azo dyes from being adsorbed or biodegraded.

In the aforementioned ETAD study into the environmental fate of dyestuffs, it was 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.

Thus, colour removal in activated sludge systems is mostly attributed to adsorption to the sludge. This is to be expected as oxygen is often an inhibitor of azo reduction. One possible explanation for this effect is competition between oxygen and an azo compound as oxidants for electron carriers.

From this discussion, it is evident that 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, solvent) is removed through adsorption to the sludge. ETAD studies have indicated that dyes, in general, are not toxic to the bacteria (Barclay, 1994).

2.3. TREATMENT METHODS

Due to the complexity and variability of textile effluents neither chemical nor biological treatment alone has proved to be adequate for efficient removal of both colour and organic matter. A combination of more than one process is usually necessary to achieve adequate removal of all contaminants rendering adverse effects to receiving streams (Shelley *et al*, 1976).

A number of methods are available for the treatment of textile effluent to reduce its colour and organic loading. These are (Tozer, 1994):

- Coagulation
- Adsorption
- Oxidation

Each process must be evaluated for:

- Effectiveness
- Generation of by-products such as sludge or other chemicals wastes
- Relative costs
- Ease of operation.

Greater detail of the individual treatment processes is given below.

2.3.1. COAGULATION

Conventional chemical treatment consists of electrolyte addition in order to cause coagulation of the dyes and other colloidal solids, followed by precipitation. In the process, a partial decolourisation is usually observed and the COD is reduced due to suspended solids removal (Tzitzi, *et al*, 1994). The following removals were obtained by Grau (1991):

BOD_5	40-50%
COD	35-40%
Colour	80-90%

Enhanced Coagulation

A number of authors have recently published research performed on the removal of colour caused by natural organic matter (NOM) by enhanced coagulation. It is possible that this technique of improved coagulation may also have application in the treatment of textile effluent.

The major mechanisms by which NOM can be removed by coagulation involve charge neutralization of colloidal NOM, precipitation as humates or fulvates, and co-precipitation by adsorption on the metal hydroxide. The degree of NOM removal through coagulation is affected by the nature and dosage of coagulants as well as the pH. Synthetic organic cationic polymers can achieve colloidal NOM charge neutralization and possibly participate in the precipitation of humic and fulvic acids. However, they do not provide a substrate for adsorption of the organic matter. In comparison, aluminium- or iron-based coagulants can achieve colloidal destabilization, can form aluminium or iron humates and fulvates that would precipitate, and also provide a surface area for adsorption on the metal hydroxides. In addition, the formation of the aluminium or ferric hydroxide floc may also be accompanied by the entrapment of some colloidal or dissolved organics, as well as concurrently formed humates or fulvates (Crozes *et al*, 1995).

The coagulation pH affects both the inorganic coagulating species and the level of dissociation of the fulvic and humic acids. At lower pH values, the level of organics protonation increases, thus reducing the coagulant demand. The coagulating species are also more positively charged at lower pH and as a consequence, adsorption becomes more favourable, and the required coagulant dosage decreases. Under low-pH conditions, it is likely that the mechanisms of charge neutralization and co-precipitation by adsorption are enhanced. The most favourable pH for ferric coagulants for removing NOM range from 4 to 5 and for aluminium coagulants was shown to be between pH 5 and 6 (Jiang and Graham, 1996; Krasner and Amy, 1995).

From the above it appears that if the use of enhanced coagulation for the removal of NOM can be extended to dyes, then optimum coagulation should be achieved with the metal coagulants ferric chloride and alum at slightly lowered pH's in the range of 4-5 and 5-6, respectively.

2.3.2. ADSORPTION

Colour can be removed by adsorption using granular activated carbon in packed beds or powdered activated carbon (PAC). PAC without the addition of alum can provide excellent colour removal with a typical PAC dose of 100mg/l producing a light pink, with higher doses rendering the water colourless. Alum combined with PAC measurably improved colour removal, but the tests revealed several disadvantages of using this strategy in a full-scale system. Firstly, the process generated sludge that would require processing and disposal, and secondly, the chemical costs of using PAC were relatively high (Tozer, 1994).

Adsorption of colour using activated carbon requires extremely large doses, resulting in high operational costs.

2.3.3. OXIDATION

Oxidation of the textile effluent can be carried out chemically or biologically.

Chemical Oxidation

Chlorine

Investigations have shown that chlorine rapidly oxidized azo dyes, achieving significant decolourisation in seconds. After two minutes, however, colour removal efficiencies did not change measurably (Tozer, 1994). Chlorine doses of 100-160mg/l rendered textile wastewater samples nearly colourless after approximately 60 minutes, with a reaction time of less than one minute at the 160 mg/l dose. Based on changes in absorbance, colour removal was greater than 95 percent for all doses tested, while removal calculated using the ADMI colour values averaged about 80 percent. Treatment with hypochlorite, however, created a toxic environment in which chlorine residual exceeded 5 milligrams per liter.

In other research chemically precipitated wastewater samples were subjected to calcium hypochlorite with a 100 mgCl_2/l dose producing a pale yellow colour. Decolouration of reactive and acid dyes by either chlorination or ozonation was found effective, with chlorination being more efficient at lower pH (Grau, 1991; Tunay *et al*, 1996).

Hydrogen peroxide

Textile wastewater oxidised with hydrogen peroxide showed no decolouration at neutral pH values. A significant colour removal was obtained with hydrogen peroxide at pH 12 only after 24 hours (Tunay *et al*, 1996). A study on acrylic dyeing wastewaters indicated that hydrogen peroxide was not effective at both acid and alkali pH values for raw and biologically treated wastewater.

Ozone

Investigations have shown ozone to be effective for decolouration (Tozer, 1994), reducing the level of soluble organics, improving biodegradability and providing disinfection (Judkin, 1981). Ozonation can be applied to both raw and chemically precipitated textile wastewater with 50 percent colour removal being obtained on raw wastewater, and 90% additional colour removal on chemically precipitated wastewater (Tunay *et al*, 1996; Tzitzi *et al*, 1994).

Ozone has the advantage over chlorine as an oxidant in that it does not result in the formation of chlorinated oxidation by-products (eg chloroform and other trihalomethanes) (Baartman, 1997). From the above it can be concluded that hydrogen peroxide alone has little effect on colour, while large concentrations of chlorine are required, which is undesirable due to the formation of halogenated byproducts. The use of ozone is more favourable with good colour removals on both raw and treated effluent.

Biological oxidation

The possible removal mechanisms for dye compounds in the activated sludge treatment system are adsorption, biodegradation, chemical transformation, photodegradation, and air stripping (Shaul *et al*, 1985). Studies show that dyes are only very slightly biodegradable, even over an extended time period. Such stability is not surprising, since in use they are frequently required to survive exposure to body fluids (Hitz, 1978).

The chief colour removal mechanism has been found to be the flocculation and absorption of the dyestuffs on the micro-organisms or mixed liquor suspended solids. Sludge acclimated to dyes is found to give better colour removal (Tunay *et al*, 1996). The permeation of dyes through the cell membrane is the primordial rate limiting step in the microbial decolourisation of azo dyes, and sulphonic acid substitution (causing increased water solubility) seems to be an effective inhibitor of permeation (Pagga and Brown, 1986).

A study of biological treatability of several textile dyeing wastewaters found that there is a trend of more colour removal with increased organic loading which is probably due to the high cellular growth rate and associated colour adsorption at higher organic loading rates (Tunay *et al*, 1996).

Joint treatment with municipal wastewaters is considered to be the optimum alternative. In general, combined treatment with municipal wastewaters has been favoured wherever possible. Combined treatment, especially if textile wastewaters form one quarter or less of the total volume, solves many of the textile effluent treatment difficulties previously listed such as flow, alkalinity and temperature extremes and fluctuations. Decolouration is also more efficient and cheaper in joint treatment systems. Municipal wastewaters supply both nitrogen and phosphorus and the proportion between concentration of BOD and dyes is more favorable than in textile wastewaters. Total production of activated sludge is thus greater and more adsorptive capacity is available. Primary sewage solids also play a role in adsorbing dyes. Some dyes are biodegraded in the anaerobic digestion of sludge.

In spite of these positive features the final effluent is still often coloured, and it is practically impossible to estimate the decolouration efficiency of joint treatment. Even pilot experiments do not guarantee perfect prediction of decolouration. Permanent changes of palette, types of dyes and fibres introduce unpredictable stochasticity, and thus flexible pre-treatment or post-treatment is a necessity (Grau, 1991).

Dyestuffs exhibit little aerobic biodegradability and thus their removal by activated sludge is limited to adsorption onto the biomass surface as their passage through the cell wall is limited. Combined treatment with domestic sewage is optimum due to the attenuation of variations in the effluent, and the improved supply of nutrients.

2.4. NEED FOR THIS RESEARCH

The Wastewater Works (WW) has experienced problems with highly coloured final effluent for many years as a result of the highly coloured effluents from the textile industries in the area which contribute 70% of the volume of the inflow. A number of investigations have been conducted into reducing the colour in the final effluent (Healey, 1987, Healey *et al*; 1989, de Haas *et al*, 1993; Gaydon and de Haas, 1998).

Research into colour reduction at source has also been performed by the Pollution Research Group at the University of Natal, with the main emphasis being on the anaerobic decolourisation of the dyes in the textile effluent (Carliell *et al*, 1995).

The General Standard requires that the effluent be free of colour. Discussions with the Department of Water Affairs and Forestry have previously indicated that the true colour of the Sterkspruit Stream, into which the Works discharges, should serve as a basis for the effluent colour (Gaydon and de Haas, 1998). In 1997 the mean colour of the outflow was 69°H, while the mean colour of the stream was 28°H. More recently, due to an inability to comply with this colour basis, an agreement was made that the colour should not exceed 70°H with effect from November 1999.

A need thus existed to perform a comprehensive investigation into the pre-treatment of the textile effluent before discharge to sewer. The effluent from the textile mill in question was chosen because it was one of the most highly coloured textile effluents in the area, and contained reactive and disperse dyes, both of which are poorly removed in activated sludge. The effluent had an average colour of 543°H in 1998 and comprised approximately 10% of the inflow to the Works. Details of the effluent quality are given in Appendix 1.

With the increased cost of potable water in the area, an opportunity may also exist for re-use of the treated effluent for certain production processes. Experience has shown that recycled water containing impurity levels many times higher than the average incoming potable water can be successfully re-used in many dyeing processes (Judkin, 1981). However, individual case studies would need to be performed because most finishing plants handle a variety of dye classes, fiber types, and dye shades, and the implementation of a water reuse program would require a careful analysis of the chemicals and mechanisms of the wet-finishing processes.

2.5. RESEARCH OBJECTIVES

The following research objectives were set:

- Primary treatment - to identify and optimise the best means of coagulating and flocculating the constituents present in the textile effluent. The coagulants included metal salts such as alum and ferric chloride; cationic, anionic, and non-ionic polymers; and polyaluminium chloride blends.

- Secondary treatment - to identify and optimise the best means of removing the colour remaining in the effluent after the above treatment. Methods to be used included oxidation using chlorine, ozone, hydrogen peroxide, and peroxone (hydrogen peroxide/ozone).

- Tertiary treatment - to perform activated sludge treatability tests on the effluent pre-treated according to the treatment methods optimised above using oxygen uptake rate meters, and to compare this with treatability data obtained for untreated effluent.

2.6. RESEARCH METHODOLOGY

2.6.1. PRIMARY TREATMENT - COAGULATION AND FLOCCULATION

Effluent samples which had undergone pH correction, equalisation, fine screening, and settling were obtained from a major contributory textile mill (grab sampling was used to obtain samples representing the average to worst quality effluent discharged by the mill, typically dark brown/black in colour). Coagulation and flocculation was optimised by means of jar tests, using a range of coagulants, and optimising coagulation pH and mixing intensities.

2.6.2. SECONDARY TREATMENT - OXIDATION

Using the method optimised above, the effluent was coagulated and flocculated and then treated with chlorine, ozone, hydrogen peroxide, and peroxone. The chlorine and hydrogen peroxide colour removal methods were conducted using jar tests, while the ozone and peroxone methods were conducted in an ozonation column.

2.7.3. TERTIARY TREATMENT - ACTIVATED SLUDGE TREATABILITY TESTS

These were conducted on both treated effluent (using the method optimised above) and untreated effluent in dilution with chicken abattoir effluent. Activated sludge from an acclimated and a non-acclimated source were used.

The treatability tests were performed in stirred glass reaction vessels coupled to automatic oxygen uptake rate monitors. The differences in oxygen uptake between the test and control reactors were used to determine treatability.

The results from the treatability tests performed above were used to determine the improvement in the final effluent colour after treatment by activated sludge, and to assess whether the final effluent from a plant receiving pre-treated effluent was suitable for discharge into the receiving water body.

CHAPTER 3 : PRIMARY TREATMENT - COAGULATION AND FLOCCULATION

Samples of textile effluent were obtained from the final discharge point at the textile mill in Hammarsdale. At this point the effluent had been pH corrected to approximately pH 7, mixed in an equalisation tank and passed through a settling tank to remove settleable fibres.

3.1. INITIAL COAGULATION EXPERIMENTS

In an initial survey the textile effluent was coagulated with alum and ferric chloride to determine which was the most effective in terms of colour and COD removal, cost and operability. The general coagulation method used is given in Appendix 1, with deviations being indicated in the text below.

3.1.1. COAGULATION WITH ALUM

Effluent samples were dosed with alum doses of 100, 200, 400, 600, 800, and 1000mg/l. All samples were pH corrected before alum addition such that the pH after alum addition was approximately 7. Once the optimum dosage had been established at pH 7, the same dosage was used at pH's of 5, 6, and 8 to establish the influence of pH on colour and COD removal, and floc quality. Having established the optimum pH the alum dosage was once again optimised.

3.1.2. COAGULATION WITH FERRIC CHLORIDE

Effluent samples were dosed with ferric chloride doses of 100, 200, 400, 600, 800, and 1000mg/l. All samples were pH corrected before ferric addition such that the pH after the ferric chloride addition was approximately 5, as a result of the coagulation experiments conducted with alum and work on enhanced coagulation by other researchers (Jiang and Graham, 1996) which showed improved colour removal at lower pH. Once an optimum ferric chloride dose had been established at pH 5, textile effluent was dosed with ferric chloride at that concentration at pH's of 6, 7 and 8, to investigate the influence of pH.

3.2. OPTIMISATION OF COAGULATION USING FERRIC CHLORIDE

The initial flocculation tests showed that ferric chloride produced a floc in the effluent at a dose of 200mg/l at pH 5. Since this was the lowest dose of any of the coagulants which achieved coagulation it was decided to optimise the coagulation parameters for ferric chloride. A preliminary experiment also showed greatly improved coagulation when 2mg/l R150 was added in conjunction with 200mg/l ferric chloride. The optimisation thus included ferric chloride dose, R150 dose, and mixing times.

3.2.1. FERRIC CHLORIDE DOSE OPTIMISATION

Effluent samples were dosed with ferric chloride doses of 50, 100, 150 and 200mg/l. The effluent samples had already been pH corrected to a final pH of 5. A constant 2mg/l R150 dose was added after the first 1 minute of rapid mixing.

At the completion of the slow stirring, the samples were allowed to settle in the beakers so that the floc size and ease of settling could be observed.

3.2.2. R150 DOSE OPTIMISATION

A constant 200mg/l dose of the ferric chloride was made to effluent samples which had been pH corrected for a final pH of 5. R150 doses of 0.5, 1.0, 1.5, and 2.0mg/l were added to the samples as before. A further rapid mix period of 2 minutes was allowed before commencing the slow stir.

3.2.3. DETERMINATION OF SLUDGE CONCENTRATION

An effluent sample was flocculated with 200mg/l ferric chloride and 1.5mg/l R150. The flocculated sample was transferred to a separating funnel and allowed to settle as before. The separating funnel was marked at the sludge - water interface and the sludge was then carefully removed to a measuring cylinder, and the supernatant retained in a beaker. The separating funnel was then filled with water to the mark made at the sludge - liquid interface and the water subsequently run into a measuring cylinder, thus enabling the sludge volume to be determined.

The sludge contained in the previously mentioned measuring cylinder was adjusted to the sludge volume obtained from the mark on the separating funnel and then transferred to a pre-weighed nickel crucible. An equal volume of supernatant to that of the sludge volume was placed in a second pre-weighed crucible, to provide for correction for the high dissolved solids of the effluent. Both crucibles were then dried overnight at 105°C and weighed after cooling in a desiccator. The sludge concentration was then calculated.

3.2.4. OPTIMISATION OF FERRIC CHLORIDE AND R150 MIXING TIMES

Although floc formation in the previous experiment had been extremely good, the following was observed:

- When the mixing time after the ferric chloride addition was reduced, colour removal deteriorated.
- The large floc formed shortly after the addition of the R150 tended to decrease in size during the flash mix.

An investigation was thus conducted into optimising the mixing times for the both ferric chloride and R150, in order to obtain optimum colour removal, a large floc size and hence improved settling.

Ferric Chloride Mixing Time Optimisation

Effluent samples were dosed with 200mg/l ferric chloride after pH adjustment and then mixed at 300rpm for 30s, 60s, and 120s. The samples were then dosed with 1.5mg/l R150 and mixed at 300rpm for a further 2 minutes whereafter they underwent slow mixing as before. The samples were then allowed to settle in the beakers before sampling the supernatant. Observations were also made regarding the quality of the floc formation.

R150 Mixing Time Optimisation

Effluent samples were dosed with 200mg/l ferric chloride after pH adjustment, and then mixed at 300rpm for 60s. The samples were then dosed with 1.5mg/l R150 and mixed at 300rpm for 30s, 60s and 120s whereafter they underwent the usual slow mixing. Observations were made regarding the quality of the floc formation and ease of settling.

3.3. SAMPLING AND ANALYSIS

Supernatant samples were analysed for pH, conductivity, colour, and COD. Blank samples were included for analysis.

3.4. RESULTS AND DISCUSSION

3.4.1. INITIAL COAGULATION EXPERIMENTS

Coagulation with alum

The initial experiment at pH 7 showed that coagulation was achieved at alum doses of 400ml and higher. Colour removal increased with the alum dose from 47% at 400mg/l to 74% at 1000mg/l, as shown below. The correlation coefficients for COD and colour removal were found to be 0.998 and 0.897 respectively.

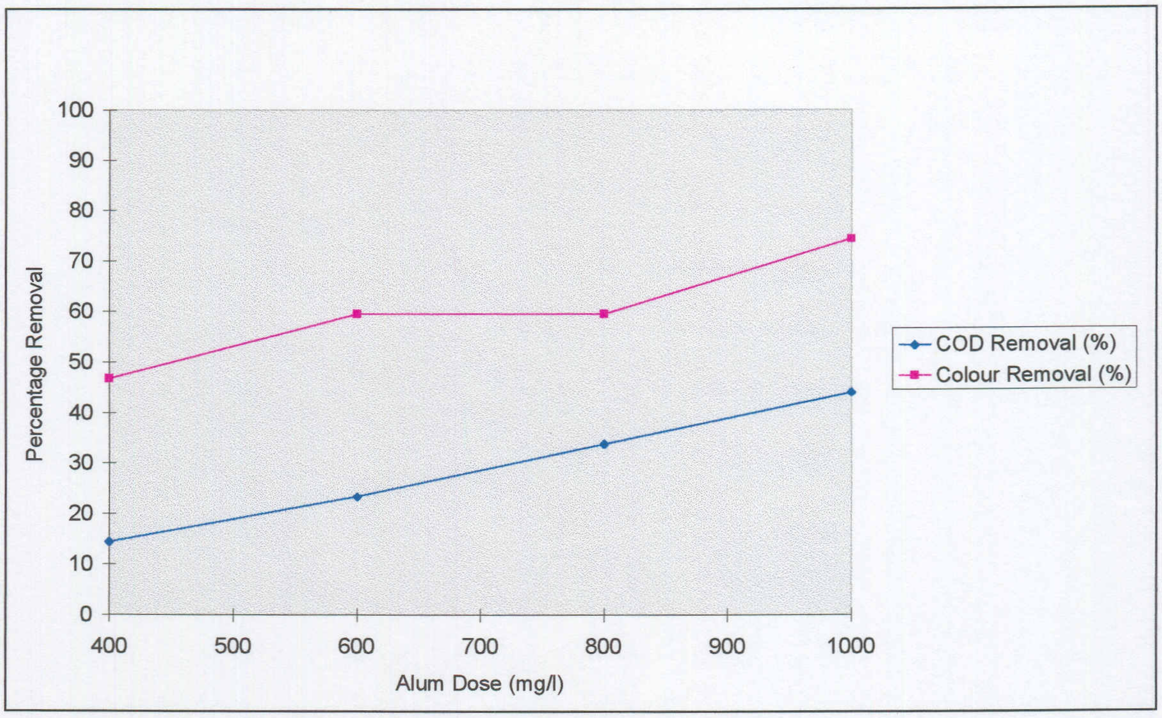

Figure 3.1 : Colour and COD removal with alum.

The results of the experiment in which the alum dose was held constant at 400mg/l and the pH varied are shown graphically below.

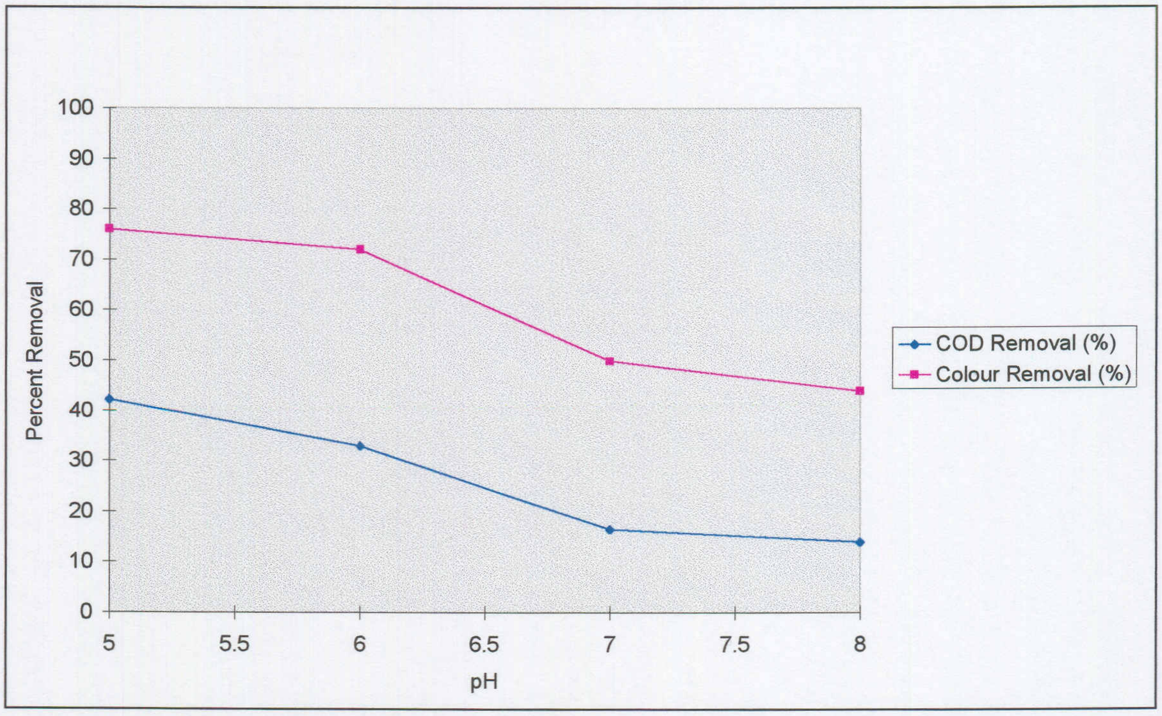

Figure 3.2 : Colour and COD removal with varying pH at an alum dose of 400mg/l.

From this it is evident that greatly improved colour and COD removals were obtained by reducing the pH to 5. The correlation coefficients for COD and colour removal were 0.937 and 0.922 respectively. Attempts to coagulate the textile effluent at pH 5 using lower alum doses were not successful. It was however observed that at pH 5 the incremental increase in colour and COD removal with increased alum dose was far smaller than at pH 7. This can be observed in Figure 3.3 below.

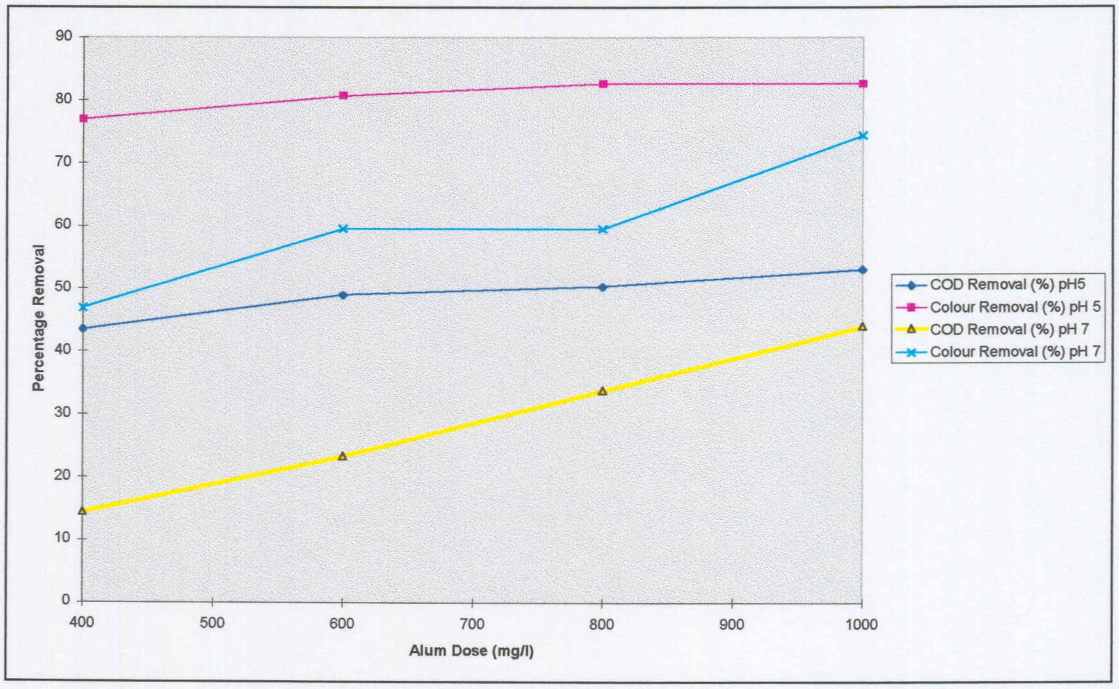

Figure 3.3 : Colour and COD removal with alum at pH 5 and 7.

From the above experiments it was clear that optimal colour and COD removal from the textile effluent was obtained when an alum dose of 400mg/l was applied at pH 5. Alum doses of less than 400mg/l at pH 5 did not produce a floc.

Coagulation with ferric chloride

Treatment of the effluent with a ferric chloride dose of 200mg/l at pH 5 produced good colour and COD removal, but the quality of the floc was poor due to small size and unsatisfactory settleability. A satisfactory floc was produced at dosages of 400mg/l and higher. The results of this experiment are shown graphically below together with the alum results for comparison.

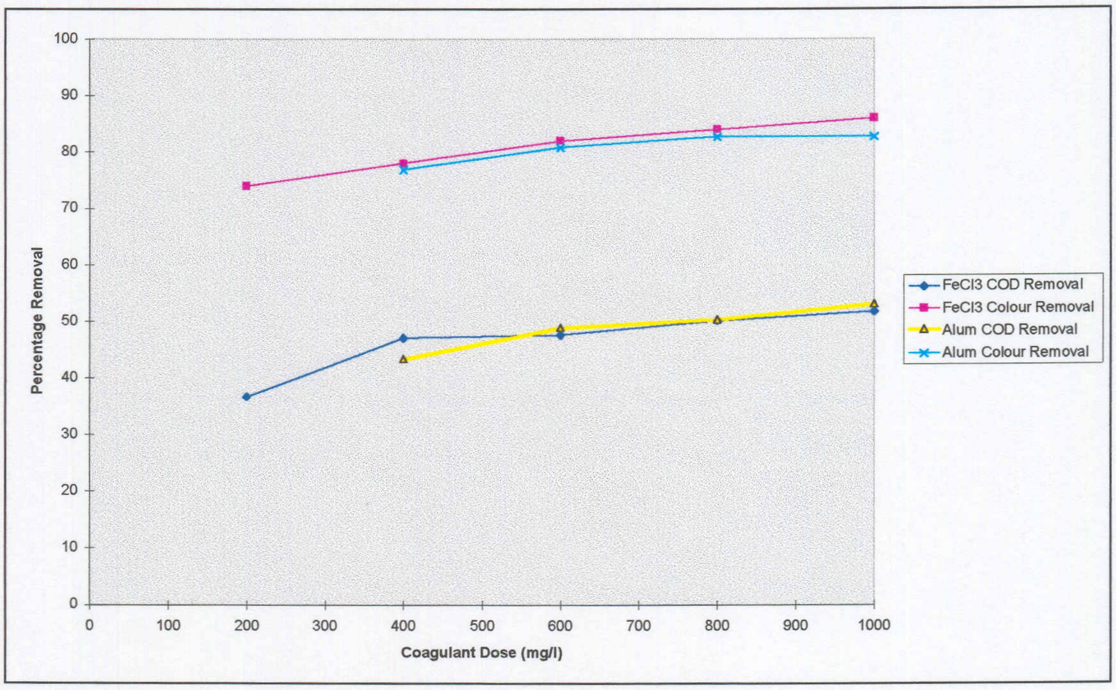

Figure 3.4 : Colour and COD removal at pH 5 using ferric chloride and alum.

The correlation coefficients for COD and colour removal with ferric chloride are 0.792 and 0.970 respectively.

The results of the experiment to investigate the influence of pH are shown graphically below.

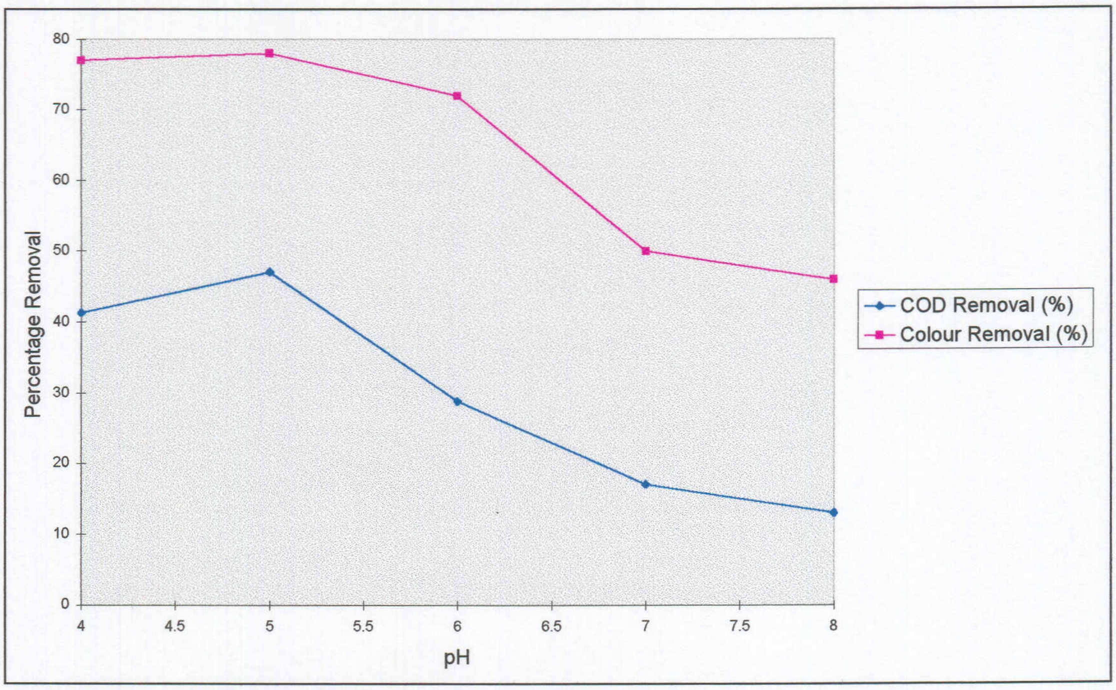

Figure 3.5 : Colour and COD removal at varying pH's using a constant ferric chloride dose of 400mg/l.

It is obvious from the graph that colour and pH removal are optimised at pH 5. The ferric chloride coagulation experiments showed that in order to produce a good floc at pH 5 a dose of 400mg/l was required. It was however possible to produce a poorer quality floc at a dose of 200mg/l.

From the above experiments it can be concluded that while both alum and ferric chloride produce a good floc at a dose of 400mg/l at pH 5, ferric chloride was able to produce a somewhat poorer quality floc at a dose of only 200mg/l with only a very small decrease in colour and COD removal.

A summary of the colour and COD removal efficiencies are given in Table 3.1.

Table 3.1 : COD and colour removals at pH 5 using alum and ferric chloride.

Coagulant	Colour Removal (%)	COD Removal (%)
400mg/l alum	77	43
400mg/l ferric chloride	78	47
200mg/l ferric chloride	74	37

Using these results it was decided to pursue the use of ferric chloride at a dose of 200mg/l and further optimise the coagulation and flocculation in order to improve the quality of the floc and thus ease of settling.

3.4.2. OPTIMISATION OF COAGULATION USING FERRIC CHLORIDE

Ferric chloride dose optimisation

The results of this experiment are shown in Table 3.2 below.

Table 3.2 : Quality of floc at various ferric chloride doses.

$FeCl_3$ dose (mg/l)*	Observations
50	No floc formation
100	Poor floc formation and colour removal
150	Poor floc formation and colour removal
200	Good floc formation and good colour removal

*A constant dose of 2mg/l R150 was used.

It was thus decided that a minimum dose of 200mg/l ferric chloride would be maintained and that the R150 dose should be optimised.

R150 dose optimisation

The results of this experiment are shown in Table 3.3.

Table 3.3 : Results of analysis for sludge volumes and floc quality observations.

R150 dose (mg/l)*	Sludge Volume ml/l	Observations
0	92	
0.5	37	Poor agglomeration
1.0	33	Poor agglomeration
1.5	35	Best agglomeration
2.0	35	Good agglomeration

* A constant dose of 200mg/l ferric chloride was used.

It was obvious that the optimum R150 dose was 1.5mg/l and the sludge volume reduction using R150 was outstanding with the sludge volume approximately one-third of the volume without R150 dosing. The R150 dose proved to be satisfactory in all subsequent coagulations.

Results for the raw effluent were as follows:
Colour (°H) 530
Conductivity (mS/m) 479
COD (mg/l) 927

The analytical results are shown graphically below:

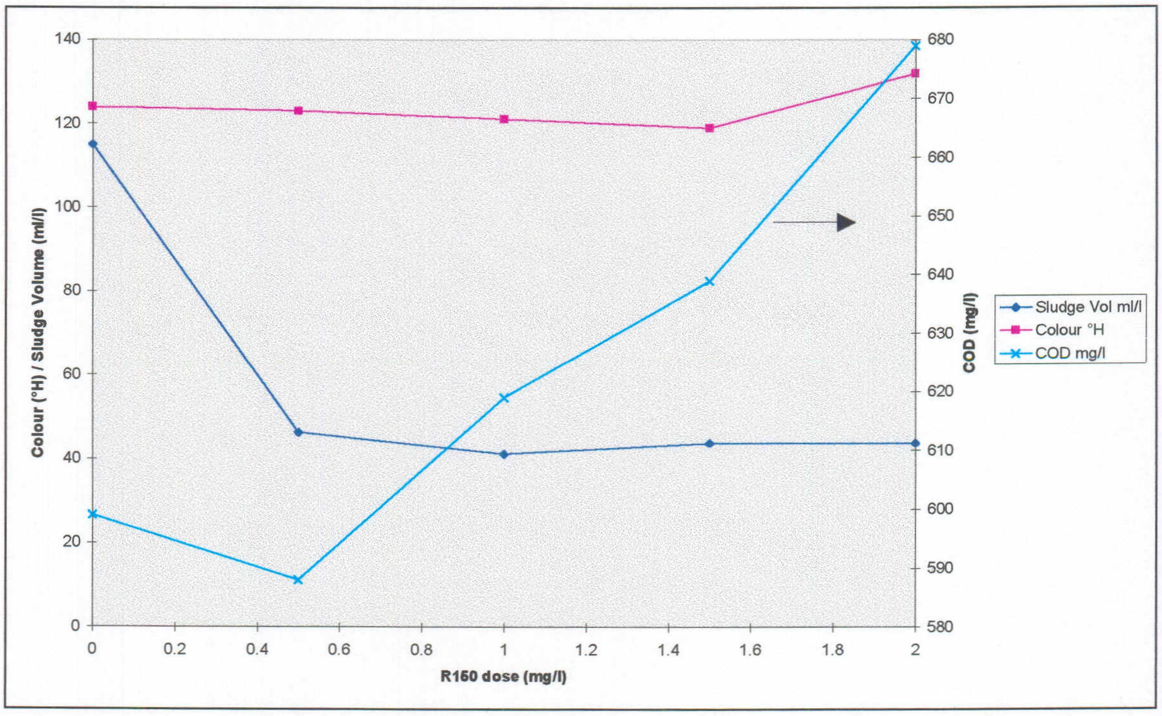

Figure 3.6 : Sludge volume, colour, and COD using R150.

The results can be summarised as follows:

- The best floc formation occurred at a R150 dose of 1.5mg/l.
- The sludge volumes are substantially reduced at all doses of R150.
- The dosing of R150 had little influence on the conductivity (as may be expected).
- The COD increased from 599mg/l with no R150 added to 639mg/l with 1.5mg/l R150 addition. This COD increase is attributed to the high COD of the polyacrylamide (a 2mg/l dose of R150 in 800ml water gives a COD of 111mg/l).
- The colour increased slightly at the highest R150 dose. The reason for this is unknown, as it does not follow the general trend.

Sludge concentration determination

This experiment showed that the sludge concentration, after correction for TDS, was 0.61% (m/v). With a sludge volume of 50ml/l and an effluent volume of approximately 1M*l*/day the sludge production would be approximately 50m^3 per day. If this could be de-watered by centrifuge to 20% (m/v) this would provide for a volume reduction to 1.53m^3 after de-watering.

Optimisation of ferric chloride and R150 mixing times.

Ferric chloride mixing time optimisation

Table 3.4 below shows the observations made during the experiment.

Table 3.4 : Floc quality and settling.

$FeCl_3$ mixing time (s) at 300rpm ($G \approx 260\ s^{-1}$) G.t values in brackets	**R150 mixing time (s) at 300rpm ($G \approx 260\ s^{-1}$)**	**Slow mixing time (min) at 40rpm ($G \approx 17\ s^{-1}$)**	**Floc Formation**	**Settling**
30 (7800)	120	15	Small floc	Fine hanging floc
60 (15600)	120	15	Large floc	Good
120 (31200)	120	15	Large floc	Good

The analytical results are shown in Table 3.5 below:

Table 3.5 : Results of analysis for colour and COD.

$FeCl_3$ mixing time (s) at 300rpm ($G \approx 260\ s^{-1}$) G.t values in brackets	**R150 mixing time (s) at 300rpm ($G \approx 260\ s^{-1}$)**	**Slow mixing time (min) at 40rpm ($G \approx 17\ s^{-1}$)**	**Colour (°H)**	**COD (mg/l)**
Blank			520	1001
30 (7800)	120	15	119	634
60 (15600)	120	15	122	674
120 (31200)	120	15	112	645

The results show that, while the colour and COD removal efficiencies are essentially independent of the mixing times used, the quality of the floc formation was poor at mixing times of less than 60s.

R150 mixing time optimisation

Table 3.6 shows the observations made during the experiment.

Table 3.6 : Floc quality and settling.

$FeCl_3$ mixing time (s) at 300rpm ($G \approx 260\ s^{-1}$)	**R150 mixing time (s) at 300rpm ($G \approx 260\ s^{-1}$) G.t values in brackets**	**Slow mixing time (min) at 40rpm ($G \approx 17\ s^{-1}$)**	**Floc Formation**	**Settling**
60	30 (7800)	15	Large floc	Good
60	60 (15600)	15	Medium floc	Good
60	120 (31200)	15	Small floc	Good

The analytical results are shown below:

Table 3.7 : Results of analysis for colour and COD.

$FeCl_3$ mixing time (s) at 300rpm ($G \approx 260\ s^{-1}$)	**R150 mixing time (s) at 300rpm ($G \approx 260\ s^{-1}$) G.t values in brackets**	**Slow mixing time (min) at 40rpm ($G \approx 17\ s^{-1}$)**	**Colour (°H)**	**COD (mg/l)**
Blank			520	1001
60	30	15	113	645
60	60	15	113	658
60	120	15	120	630

The results once again show that the colour and COD removal are independent of the R150 mixing time. However, floc quality was best at the shortest mixing time of 30s.

It was subsequently observed in the laboratory that the 15 minute slow mixing time at 40 rpm was unnecessary and could be omitted. It was also observed that the floc was prone to a degree of breakup when transferred from one vessel to another which should be borne in mind during design of hydraulic conduits.

The results of the above experiments show that the colour and COD removals were not adversely affected by varying the mixing parameters within the ranges used. However best floc formation and settling was achieved when the ferric chloride mixing time was 1-2 minutes and the R150 mixing time was 30s. A slow mix was not necessary.

3.5. PRIMARY TREATMENT OF EFFLUENT - CONCLUSIONS

From the above investigation it can be concluded that both alum and ferric chloride produced satisfactory coagulation of the effluent at a dose of 400mg/l. Ferric chloride was, however, able to produce a floc, albeit of a poorer quality, at 200mg/l. The optimum pH for coagulation was found to be pH 5 which is in agreement with the research conducted by Jiang and Graham, (1996) and Krasner and Amy (1995).

The use of a polymeric polyacrylamide coagulant, R150, in conjuction with the ferric chloride improved the floc size and settleability, and reduced the sludge volume. The colour and COD removals achieved at the optimum ferric chloride (200mg/l) and polyacrylamide (1.5mg/l) doses were in the range of 70-80% and 30-40%, respectively. This in agreement with the research conducted by Grau (1991).

Optimisation of the ferric chloride and polyacrylamide mixing times showed that best floc quality, in terms of size and settleability, was achieved at a Camp's number (G.t) of between 15600 and 31200 for the ferric chloride, and 7800 for the ferric chloride and polyacrylamide combination.

CHAPTER 4 : SECONDARY TREATMENT - OXIDATION

4.1. OXIDATION WITH CHLORINE

A chlorine working solution was made up by diluting a commercial stock solution tenfold and titrating with a sodium thiosulphate solution of known concentration to determine chlorine concentration. The concentration of the stock solution was found to be 38883.6mg/l and hence the working solution concentration was 3888.4mg/l.

Effluent samples (pH adjusted to 6.5 to ensure that most of the chlorine was present as the HOCl species) were treated with chlorine doses of 2, 4, 8, 12, 16, and 20mgCl_2/l and stirred for 30 minutes. A spatula load of sodium thiosulphate was then added and the samples stirred for a further 5 minutes to neutralise the chlorine.

4.2. OXIDATION WITH HYDROGEN PEROXIDE

A hydrogen peroxide working solution was made up by diluting a commercial stock solution tenfold and titrating with a sodium thiosulphate solution of known concentration to determine the hydrogen peroxide concentration.

In order to establish the optimum pH for the oxidation reaction 20mg/l hydrogen peroxide doses were added to 200ml effluent samples with pH's of 5, 7 and 9. The samples were then stirred and allowed to stand for 30 minutes before a spatula tip of sodium thiosulphate was added to neutralise the hydrogen peroxide. The samples were analysed for colour to determine the optimum pH for colour removal.

200ml samples (pH adjusted to 5) were treated with hydrogen peroxide doses of 10, 20, 30, 40, and 50mgH_2O_2/l and well stirred. The samples were then allowed to stand as before, and the residual hydrogen peroxide neutralised thereafter.

4.3. OXIDATION WITH OZONE

A 10 liter sample of effluent at pH 7 was ozonated in an ozonation column as shown in Figure 4.1. Doses of 10, 20, 30, 40, and 50mg/l ozone were applied.

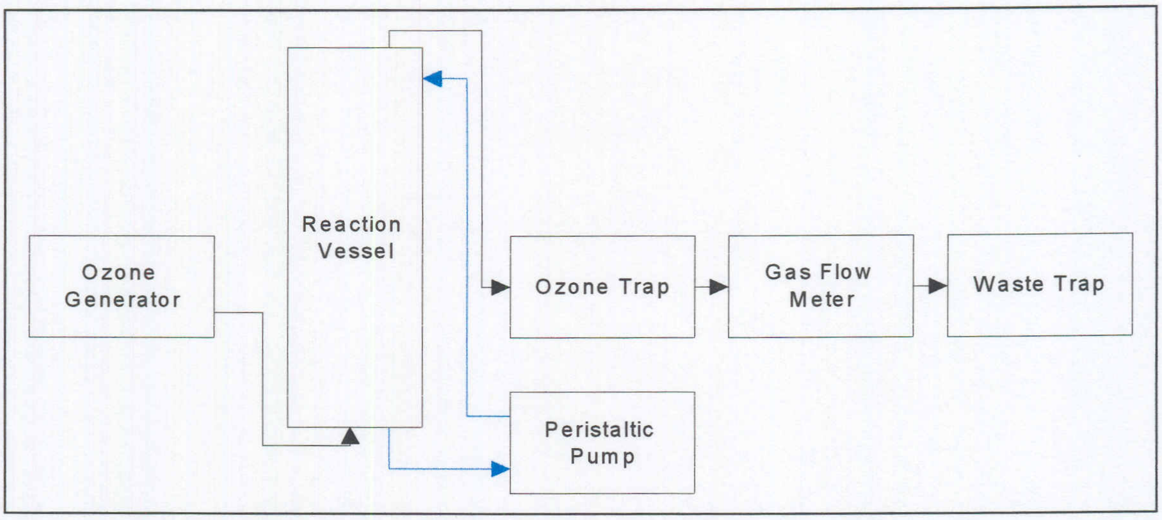

Figure 4.1 : Diagram of ozonation apparatus.

Ozone was produced by passing pure oxygen through a Sorbios ozone generator. The ozone was then introduced into the column filled with sample through a glass frit at the bottom of the column. The sample was re-circulated through the column in a counter-current direction with respect to the rising ozone. The waste gas stream above the sample was released to the atmosphere via an ozone trap (containing potassium iodide solution) and a gas flow meter (Gaydon and de Haas, 1998).

Prior to ozonation of the sample, the ozone concentration of the gas stream was measured by ozonating a potassium iodide solution contained in the column and then titrating the solution with sodium thiosulphate of known concentration.

The potassium iodide solution contained in the ozone trap after the column reacts with any un-reacted ozone, and this was measured by titration. The gas flow meter measured the volume of gas which passed through the system, and together with the concentration of ozone in the gas stream is used to determine the ozone dose.

Due to the limited volume of sample available fresh columns could not be used for each ozone dosage. Instead a 250ml sample was withdrawn from the column as each dosage was reached. During the sample withdrawal, the ozone stream was diverted to waste. The ozone trap was also titrated after each ozone dose to measure the un-reacted ozone.

4.4. OXIDATION WITH PEROXONE (HYDROGEN PEROXIDE / OZONE)

A 10 liter sample of effluent at pH 7 was treated with hydrogen peroxide and ozone (collectively called peroxone) in the same ozonation column as shown and described in 4.3. above. The hydrogen peroxide was added stepwise according to the ozone dose in an optimum 0.35:1 ratio (Volk *et al*, 1997) which reflects the stoichiometric ratio in the equation:

$$H_2O_2 + 2O_3 \rightarrow H_2O + 2O_2^{\bullet}$$

Doses of 3.5, 7, 10.5, 14, and 17.5mg/l hydrogen peroxide and 10, 20, 30, 40, and 50mg/l ozone (the same as in section 3.3.3. above) were applied. The ozone trap was titrated after each peroxone dose to measure the un-reacted ozone.

4.5 SAMPLING AND ANALYSIS

Samples of the oxidised effluent were analysed for colour, COD and THM's (chlorine oxidation). The absorption spectrum of the ozonated sample was measured and compared with that of a non-ozonated sample. Blank samples were included for analysis.

4.6. RESULTS AND DISCUSSION

4.6.1. OXIDATION WITH CHLORINE.

The results of analysis are shown in Table 4.1.

Table 4.1 : Results of colour analysis for chlorine oxidation.

Chlorine Dose (mg/l)	**Colour (°H)**
0	94.9
2	93.8
4	92.6
8	96.1
12	102.0
16	104.3
20	104.3

The results show that oxidation with chlorine did not reduce the colour but rather increased it slightly, with a chlorine dose of 20mg/l producing a colour increase of almost 10%. Higher chlorine doses, as shown to be effective in the literature (Grau, 1991; Tunay *et al*, 1996) were not used due to concerns regarding the formation of chlorinated by-products which are environmentally undesirable.

4.6.2. OXIDATION WITH HYDROGEN PEROXIDE.

The results of analysis are shown in Table 4.2 below.

Table 4.2 : Results of colour analysis at various pH's for hydrogen peroxide oxidation.

pH	**Hydrogen Peroxide Dose (mg/l)**	**Colour (°H)**
Blank	0	96.1
5	20	90.2
7	20	92.6
9	20	93.8

The results show that pH does not appear to have a major influence on the colour removal, with very little difference in colour removal across the range of pH's used. In view of the results showing slightly better colour removal at pH 5, which is also the pH at which the coagulation was performed, it was decided to use this pH in the remainder of the experiments with hydrogen peroxide.

The results of the experiments performed using varying hydrogen peroxide doses are shown in Table 4.3.

Table 4.3 : Results of colour analysis for hydrogen peroxide oxidation

pH	**Hydrogen Peroxide Dose (mg/l)**	**Colour (°H)**
5	0	96.1
5	10	94.9
5	20	93.8
5	30	91.4
5	40	94.9
5	50	90.2

The results show that the addition of hydrogen peroxide produced very little colour reduction even at high doses, with a 50mg/l dose of hydrogen peroxide producing only a 6% colour reduction.

4.6.3. OXIDATION WITH OZONE.

The results of analysis are shown in Table 4.4.

Table 4.4 : Results of analysis for ozone oxidation.

Ozone Dose (mg/l)	Colour (°H)	COD (mg/l)
0	122	281
4	122	267
8	114	273
12	107	263
16	94	259
20	82	263
30	63	246
40	54	245
50	48	251

The colour results are shown graphically in Figure 4.2 below.

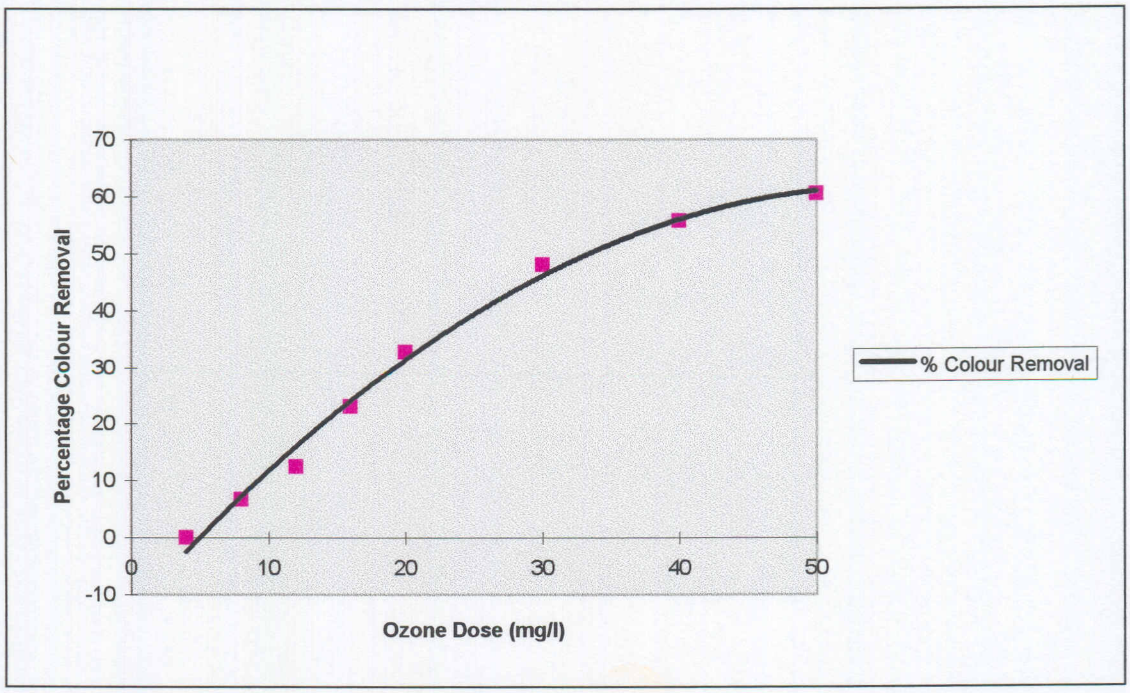

Figure 4.2 : Colour removal with ozonation.

The above graph shows a gradual increase in colour removal up to the maximum ozone dose of 50mg/l, where the colour removal is 61%. The colour removal curve, however, flattens off above a dose of 30mg/l suggesting that this is the optimum dose. If curve fitting is applied to the data then the trendline shown is obtained using a second order polynomial, with an R^2 coefficient of 0.9932. The polynomial expression defining the fit is:

$$y = -0.0244x^2 + 2.687x - 12.821$$

where
y = percentage colour removal
x = ozone concentration (mg/l)

It was also noticed that the effluent changed in hue from a green /brown hue to a more orange hue during the ozonation. Figure 4.3 shows the visible light absorption spectra before and after the ozonation.

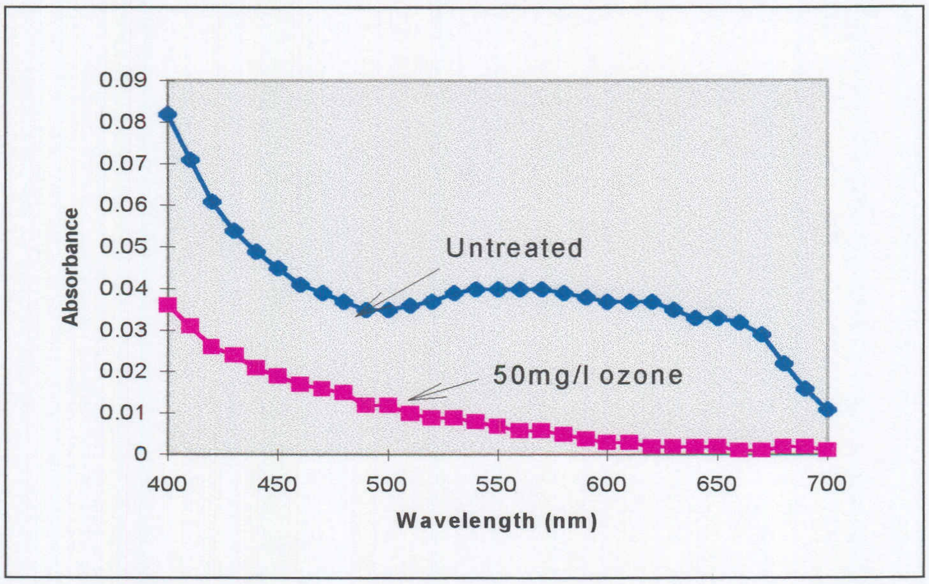

Figure 4.3 : Absorbance spectra for untreated and ozonated samples.

The graph shows that the reduction in absorbance in the range 400-500nm was between 56 and 66 percent, while the reduction in absorbance in the range 510-700nm was between 70 and 90 percent. This change in relative absorbances results in the change in hue of the visible colour.

The COD results are shown graphically in Figure 4.4.

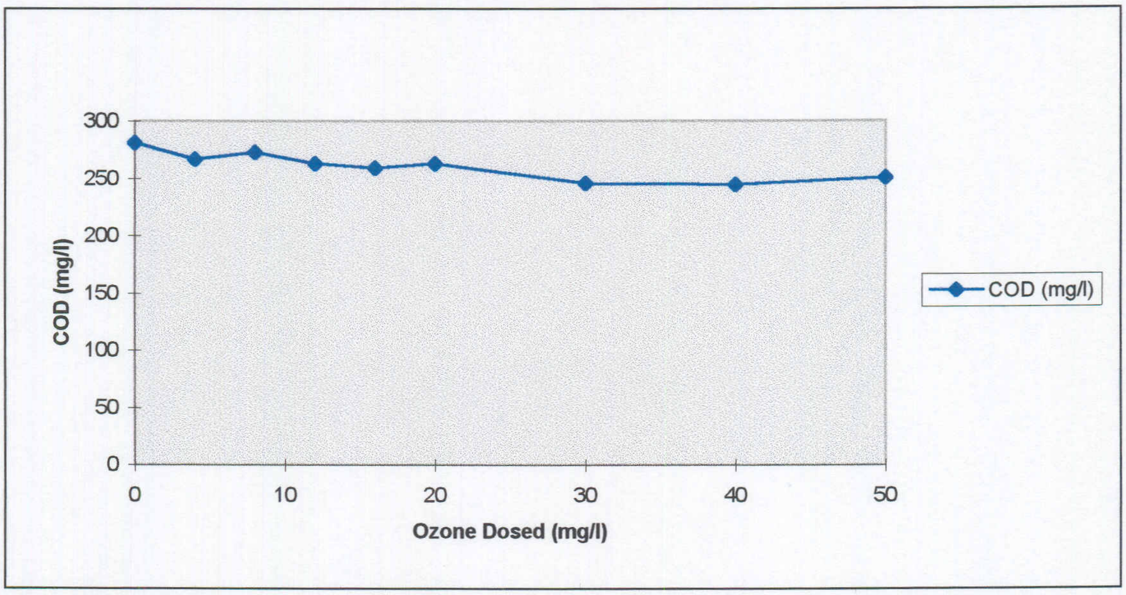

Figure 4.4 : COD with ozonation.

The COD results show a very slight downward trend with increased ozone concentration, indicating that the molecules in the effluent were not undergoing full combustion, but merely being fragmented.

4.6.4. OXIDATION WITH PEROXONE (HYDROGEN PEROXIDE/OZONE).

The results of analysis are shown in Table 4.5. It is important to note that in all cases hydrogen peroxide was added in a 0.35:1 ratio to the ozone dose given.

Table 4.5 : Results of analysis for peroxone oxidation.

Ozone Dose (mg/l)	**Colour (°H)**	**COD (mg/l**
0	117	253
4	123	259
8	113	247
12	107	230
16	90	225
20	83	263
30	64	234
40	60	213
50	52	252

The colour results are shown graphically in Figure 4.5.

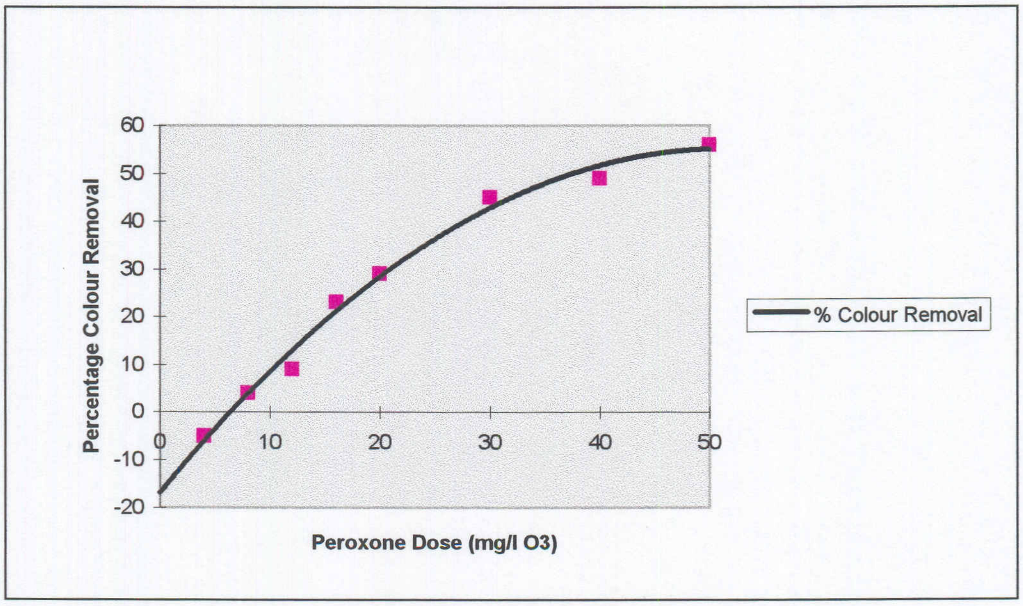

Figure 4.5 : Colour removal with peroxone oxidation.

The graph shows a similar increase in colour removal to that obtained with ozone above, with the colour removal being 56% at a peroxone dose of 50mg/l (with a corresponding hydrogen peroxide dose of 17.5mg/l). Curve fitting produces the following expression for colour removal, with an R^2 coefficient of 0.9906:

$$y = -0.0275x^2 + 2.817x - 16.885$$

where

y = percentage colour removal

x = ozone concentration (mg/l)

It was once again noticed that the effluent changed its hue from a green/brown hue to a more orange hue during the peroxonation as observed during the ozonation.

The COD results are shown graphically in Figure 4.6.

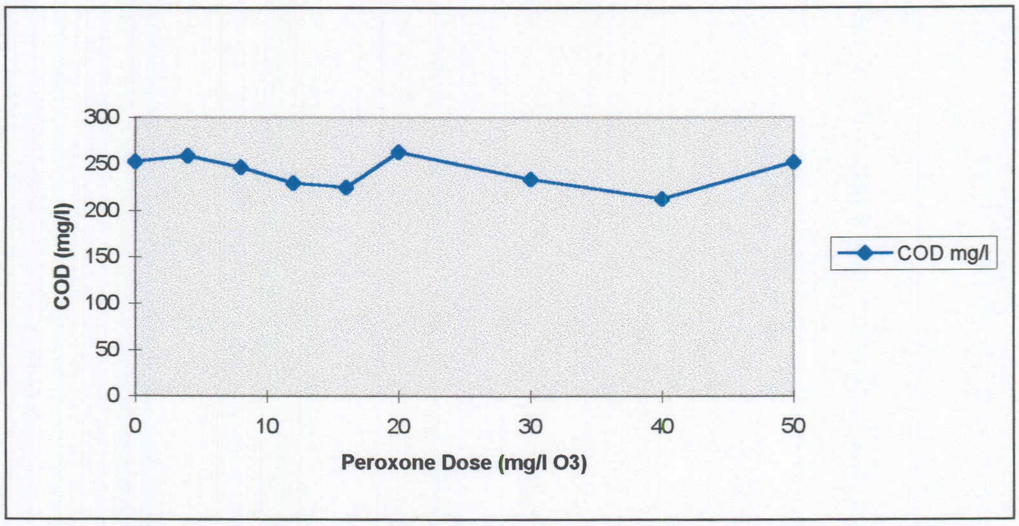

Figure 4.6 : COD with peroxone oxidation.

The COD results show no discernible trend as a function of peroxone dose.

4.6.5. COMPARISON OF OZONATED EFFLUENT WITH EFFLUENT TREATED WITH PEROXONE

Figure 4.7 provides a comparison of the results obtained from samples treated with ozone and peroxone.

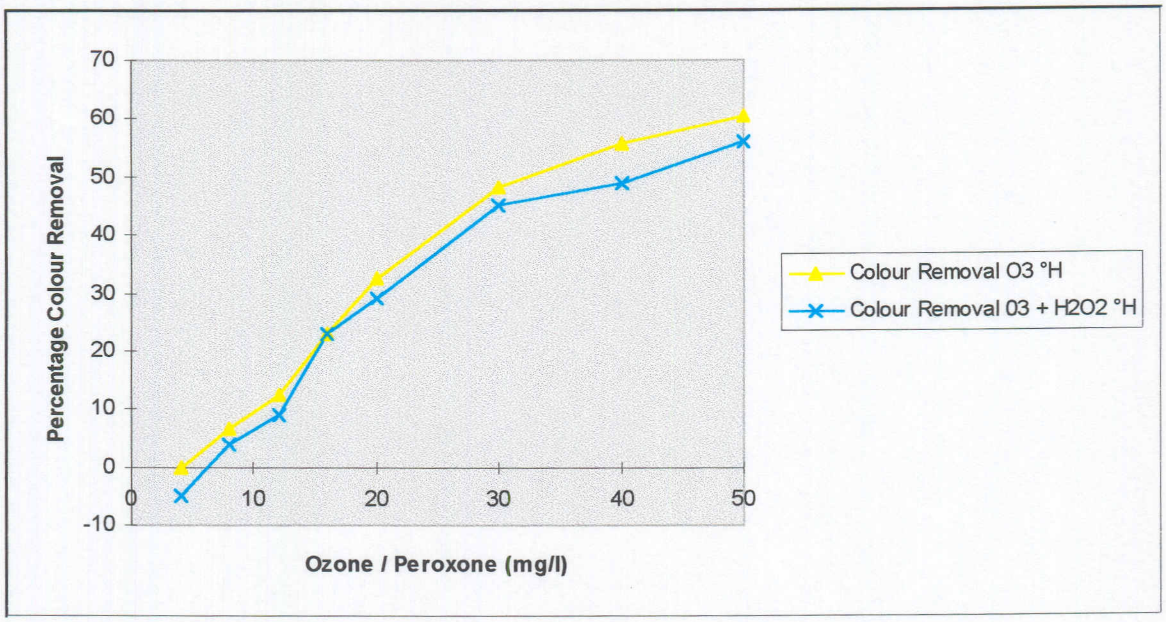

Figure 4.7 : Comparison of colour removal for ozonation and peroxonation.

The above graph shows that the use of peroxone did not result in better colour removal from the coagulated textile effluent; rather the colour removal obtained using solely ozone were marginally better. The reason for this is probably that straight ozone oxidises the dye chromophores selectively while the radicals formed in the peroxone reaction tend to attack the dye molecule indiscriminately.

4.7. SECONDARY TREATMENT OF EFFLUENT - CONCLUSIONS

The results show that the colour removal achieved using chlorine and hydrogen peroxide at the stated doses were zero and almost negligible, respectively, as indicated by Tunay *et al* (1999) and Tozer (1994).

Oxidation with ozone and peroxone produced almost identical results, with no advantage being seen in supplementing the hydrogen peroxide.

The expression for the colour removal by ozone was found to be:

$$y = -0.0244x^2 + 2.687x - 12.821$$

while that for peroxone was:

$$y = -0.0275x^2 + 2.817x - 16.885.$$

An optimum dose of 30mg/l was found to reduce colour by 48%, with the colour removal efficiency above this dose deteriorating. These results correspond well with the research performed by Tunay *et al* (1996) and Tzitzi *et al* (1994). The change in hue of the effluent, observed during ozone and peroxone oxidation, can be explained in terms of variations in absorption changes in the visible wavelength range of 400-700nm.

CHAPTER 5 : TERTIARY TREATMENT - BIOLOGICAL TREATMENT

5.1. ACTIVATED SLUDGE BATCH TESTS

Activated sludge treatment batch tests were conducted for the raw, coagulated (200mg/l ferric chloride, 1.5mg/l R150), and coagulated and ozonated (30mg/l) effluent, using sludge from the Hammarsdale WWW and Darvill WWW. Two sets of batch tests were run - one for the Hammarsdale WWW activated sludge and the other for the Darvill WWW activated sludge. Each set of batch tests consisted of three separate batch tests, one for each kind of effluent.

Each batch test was performed by mixing a 1.5*l* sample of return activated sludge (RAS) with a 1.5*l* sample of feed composed of a 70:30 mix of effluent and chicken abattoir effluent (the same ratio mix as in the inflow to the Works). The chicken abattoir effluent was added to ensure the availability of a large amount of biodegradable COD to promote rapid biomass growth which is indicated in dye absorption (Treffry-Goatley *et al*, 1991).

The RAS was washed with an isotonic solution of ultrapure water to remove the residual refractory colour in the liquor. This was performed by splitting the 1.5*l* sample between four centrifuge vessels and centrifuging at 3000rpm ($g \approx 1800$) for 5 minutes. The supernatant was carefully decanted and discarded, and 200ml isotonic water (200mS/m sodium chloride solution for the Hammarsdale RAS) added and well mixed to re-suspend the sludge. The RAS was then centrifuged again and the washing procedure repeated a total of three times. The washed RAS was then made up to the original volume using the isotonic water solution.

The washed RAS was then placed in a 5*l* glass beaker fitted with a sampling tap at the base, and this was in turn placed on a magnetic stirrer. A stirrer bar was added and the mixture stirred slowly to maintain the RAS in suspension. The 1.5*l* mixture of the textile and abattoir effluent was then added.

The mixture was then subjected to the same aeration ratio as that of the Hammarsdale WWW with a 14 hour anaerobic period, followed by a 37 hour aerobic period, and finally a 13 hour anoxic period. These periods are longer than usual since the Works was designed for an inflow of 27Ml/d but currently receives only 12Ml/d. During the aerobic period aeration was performed using an airstone connected to a fishtank pump, and controlled by a UCT dissolved oxygen monitor. The oxygen uptake rate (OUR) data accumulated by the UCT dissolved oxygen monitors was downloaded for subsequent analysis for OUR inhibition by the effluent.

5.2. SAMPLING AND ANALYSIS

Samples of the washed RAS were taken and analysed for MLSS. A filtered sample was analysed for colour and COD. A sample of the chicken abattoir effluent was analysed for colour and COD. Samples of the raw, coagulated, and coagulated and ozonated textile effluent were taken before mixing with the abattoir effluent and analysed for colour and COD. Samples of the activated sludge (AS) mixture were taken initially, after the anaerobic period, after 12, 24, and 37 hours of aerobic treatment, and after the anoxic period. These samples were filtered through a Whatman No. 1 and analysed for colour and COD.

5.3. RESULTS AND DISCUSSION

5.3.1. INHIBITION OF ACTIVATED SLUDGE TREATMENT BY EFFLUENT

The oxygen uptake rate (OUR) data collected by the UCT dissolved oxygen monitor during the batch test using the Hammarsdale activated sludge was lost due to a power dip during the initial twelve hour period of aeration. Unfortunately this is the most important data for toxicity analysis as it is during the first few hours that toxicity is indicated by a sudden drop in the OUR of the activated sludge.

The OUR data from the batch test performed using the Darvill activated sludge, which was not acclimated to textile effluent and would thus be more inclined towards inhibition, is shown in Figure 5.1.

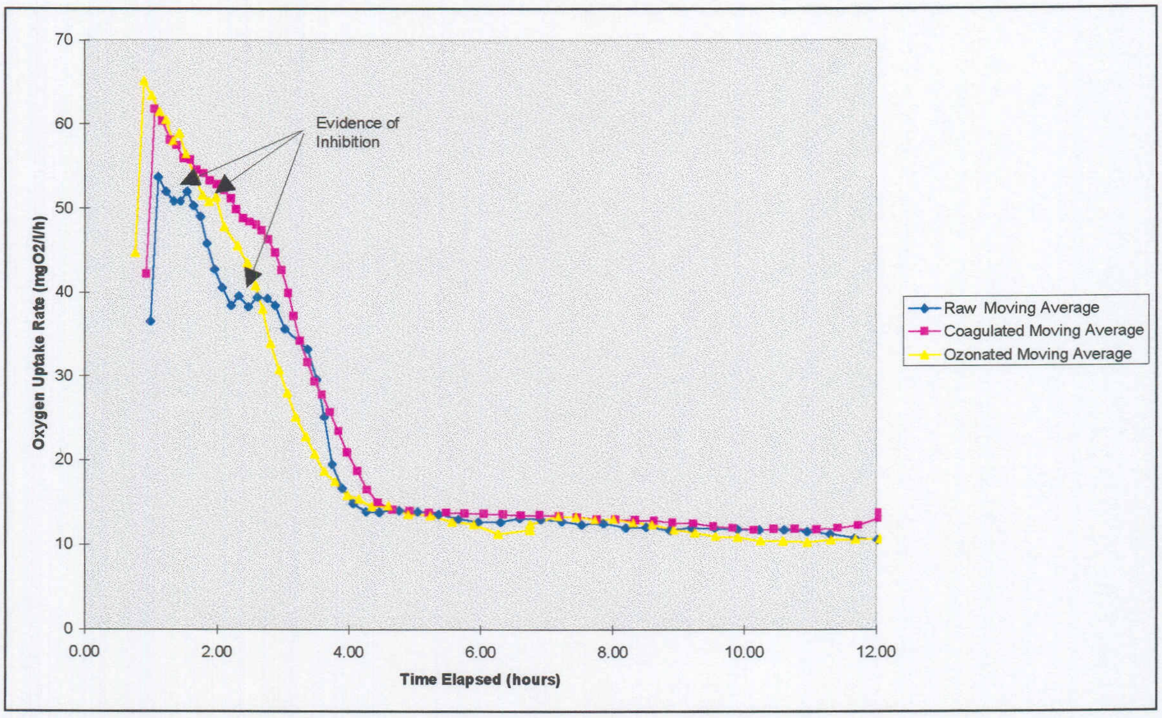

Figure 5.1 : Moving averages of the OUR data for Darvill activated sludge batch test.

The OUR data shows that the highest peak OUR was obtained by the coagulated and ozonated effluent sample, while the coagulated effluent sample gave a lower peak OUR, followed by the raw effluent sample. This indicates that the highest biodegradability was experienced with the coagulated and ozonated effluent sample and the lowest biodegradability by the raw effluent sample.

The OUR curve for the raw effluent sample, which should be more or less smooth, shows two regions in which inhibition of the activated sludge appear to have taken place. In both regions the OUR drops, steadies out or vacillates, rises again, and then continues with its normal descent.

Although this behaviour is not apparent with the coagulated effluent sample, it may be occurring with the ozonated sample where the OUR drops and then rises again rapidly.

5.3.2. COLOUR AND COD REMOVAL BY ACTIVATED SLUDGE

Hammarsdale Activated Sludge

Analysis of the RAS gave a MLSS of 9008mg/l which translates to an activated sludge concentration of 4504mg/l when mixed with the inflow. The results of analysis for colour and COD are shown in Table 5.1.

Table 5.1 : Results of analysis for colour and COD.

	Type of Textile Effluent Used in Batch Test					
	Raw		**Coagulated**		**Ozonated**	
Sample Description	**Colour (°H)**	**COD (mg/l)**	**Colour (°H)**	**COD (mg/l)**	**Colour (°H)**	**COD (mg/l)**
Textile effluent before AS	520	1073	117	238	82	268
Initial sample after mixing	172	491	59	229	49	235
After anaerobic	164	319	54	114	47	124
After 12 hours aerobic	151	184	43	73	38	93
After 24 hours aerobic	142	187	74	92	66	79
After 37 hours aerobic	126	199	71	77	61	75
After anoxic	116	141	63	75	58	76

The colour and COD results for the chicken abattoir effluent and washed RAS are shown in Table 5.2.

Table 5.2 : Results of analysis for colour and COD.

Sample Description	**Colour (°H)**	**COD (mg/l)**
Abattoir effluent before AS	240	3519
Washed RAS	18	42*

*COD not analysed due to laboratory error - assumed to be same as for Darvill RAS

The results in Table 5.1 are shown in Table 5.3 after correction for the initial colour and COD present in the return activated sludge. The correction was calculated as follows:

Colour = [(2 x measured colour) - (initial colour of RAS)]

The following assumptions (which in reality may not be completely valid) were made in applying the correction:

- No further colour is released from the AS flocs into the liquid to produce a new absorption equilibrium, and no coloured metabolites of substrate absorbed prior to the batch test are released.
- The colour due to the chicken abattoir effluent is fully removed.

The COD correction was analogous to the colour correction as were the assumptions made.

Table 5.3 : Results of analysis for colour and COD after correction for initial concentrations in RAS.

	Type of Textile Effluent Used in Batch Test					
	Raw		**Coagulated**		**Ozonated**	
Sample Description	**Colour (°H)**	**COD (mg/l)**	**Colour (°H)**	**COD (mg/l)**	**Colour (°H)**	**COD (mg/l)**
Textile effluent before AS	520	1073	117	238	82	268
Initial sample after mixing	325	940	101	416	81	428
After anaerobic	311	596	89	186	76	206
After 12 hrs aerobic	283	326	69	104	58	143
After 24 hrs aerobic	267	332	131	141	114	116
After 37 hrs aerobic	234	356	124	112	105	108
After anoxic	213	240	108	107	98	110

The results are shown graphically in Figures 5.2 and 5.3.

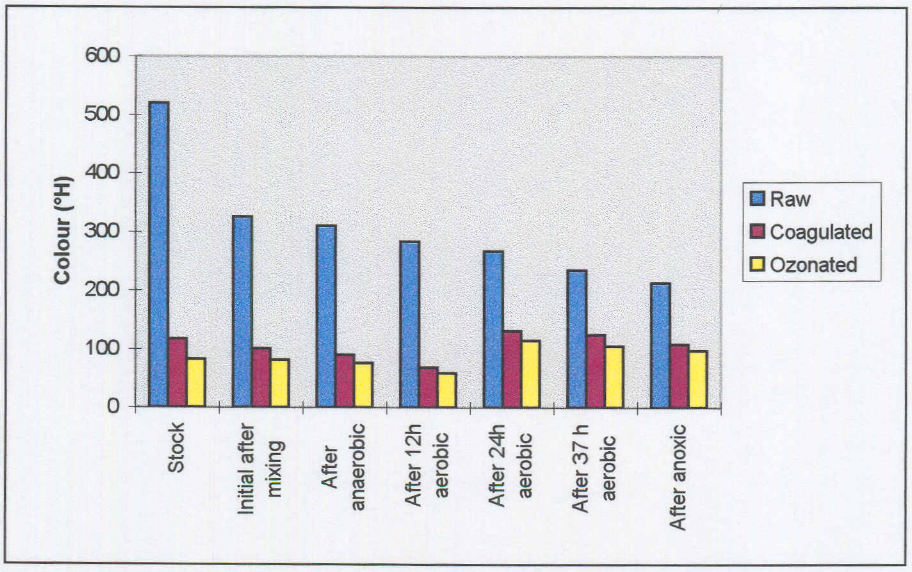

Figure 5.2 : Colour reduction during Hammarsdale activated sludge batch test.

The results show that the colour of the raw textile effluent decreased gradually from 520°H to 213°H during activated sludge treatment, while the coagulated textile effluent decreased in colour to a minimum of 69°H after the anaerobic phase and first

12 hours of aerobic treatment, but then increased once again during the remainder of the aerobic phase, before decreasing slightly during the anoxic phase. The colour of the coagulated and ozonated effluent decreased in a similar manner to that of the coagulated effluent, and reached a minimum of 58°H after the first 12 hours of aerobic treatment. The colour then increased again during the remainder of the aerobic period before decreasing slightly during the anoxic period.

The COD of the raw textile effluent decreased through the anaerobic period and the first 12 hours of the aerobic phase before rising slightly during the remainder of the aerobic phase. The COD declined significantly during the anoxic phase, with a final minimum COD of 240mg/l. The coagulated textile effluent mirrored the trend of the raw effluent, reaching a minimum of 104mg/l after the first 12 hours of aerobic treatment and then rising thereafter during the remainder of the aerobic treatment before falling to 107mg/l after anoxic treatment. The coagulated and ozonated effluent decreased in COD throughout the anaerobic and aerobic treatment phases, reaching a minimum of 108mg/l, before increasing very slightly to 110mg/l during the anoxic phase.

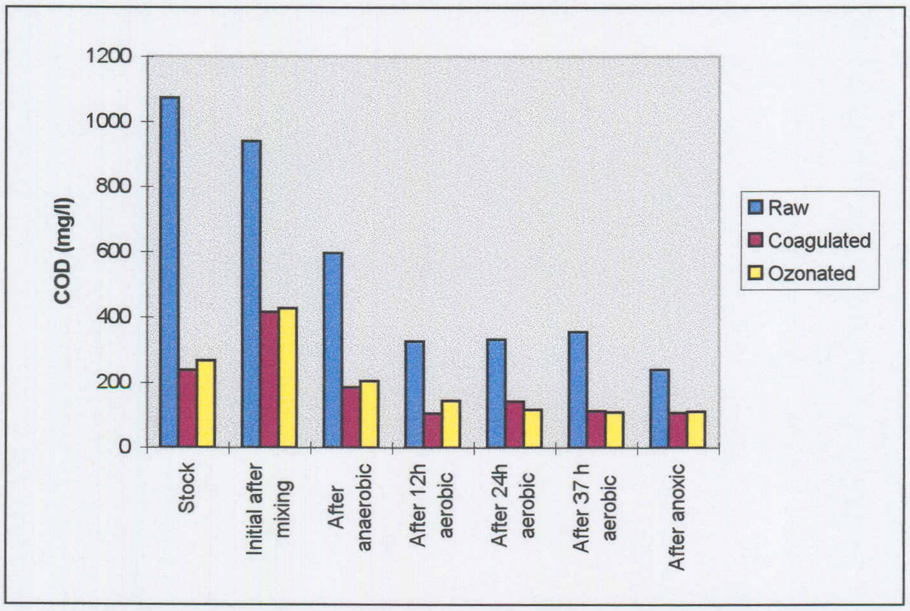

Figure 5.3 : COD reduction during Hammarsdale activated sludge batch test.

Darvill Activated Sludge

Analysis of the RAS gave a MLSS of 7000mg/l which translates to an activated sludge concentration of 3500mg/l when mixed with the inflow. The results of analysis for colour and COD are shown in Table 5.4.

Table 5.4 : Results of analysis for colour and COD.

	Type of Textile Effluent Used in Batch Test					
	Raw		Coagulated		Ozonated	
Sample Description	**Colour (°H)**	**COD (mg/l)**	**Colour (°H)**	**COD (mg/l)**	**Colour (°H)**	**COD (mg/l)**
Textile effluent before AS	514	1156	101	269	66	279
Initial sample after mixing	175	460	60	219	53	220
After anaerobic	111	324	51	143	43	141
After 12 hrs aerobic	122	176	52	81	45	89
After 24 hrs aerobic	124	162	69	69	62	87
After 37 hrs aerobic	140	194	72	96	56	76
After anoxic	135	146	70	84	57	86

The colour and COD results for the chicken abattoir effluent and washed RAS are shown in Table 5.5.

Table 5.5 : Results of analysis for colour and COD.

Sample Description	Colour (°H)	COD (mg/l)
Abattoir effluent before AS	9	3279
Washed RAS	151	42

The results in Table 5.4 are shown in Table 5.6 after correction for the initial colour and COD present in the return activated sludge.

Table 5.6 : Results of analysis for colour and COD after correction for initial concentrations in RAS.

	Type of Textile Effluent Used in Batch Test					
	Raw		**Coagulated**		**Ozonated**	
Sample Description	**Colour (°H)**	**COD (mg/l)**	**Colour (°H)**	**COD (mg/l)**	**Colour (°H)**	**COD (mg/l)**
Textile effluent before AS	514	1156	101	269	66	279
Initial sample after mixing	341	878	110	396	96	398
After anaerobic	213	606	92	244	77	240
After 12 hrs aerobic	235	310	96	121	82	137
After 24 hrs aerobic	238	282	127	97	116	131
After 37 hrs aerobic	271	346	134	151	104	110
After anoxic	261	250	130	127	106	130

The results are shown graphically in Figures 5.4 and 5.5.

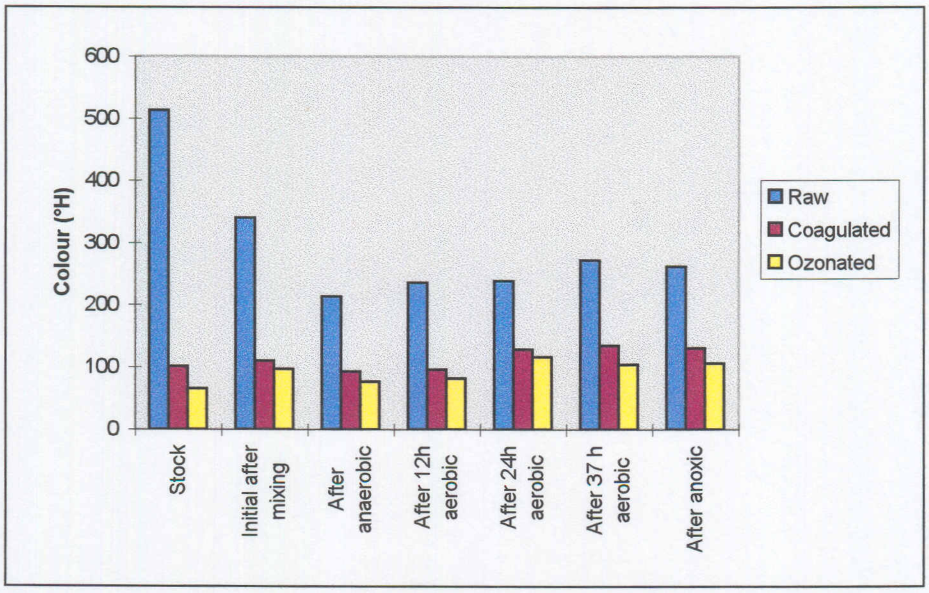

Figure 5.4 : Colour reduction during Darvill activated sludge batch test.

The colour of the raw effluent decreased to a minimum of 213°H at the end of the anaerobic period, and then increased once again to 261°H at the end of the anoxic period. The colour of the coagulated effluent followed a similar trend with a minimum of 92°H after the anaerobic phase, increasing to 130°H after the anoxic phase. The coagulated and ozonated textile effluent also followed a similar trend, with the colour reaching a minimum of 77°H after the anaerobic phase, and then rising to 104°H at the end of the aerobic phase, before increasing slightly to 104°H after the anoxic phase.

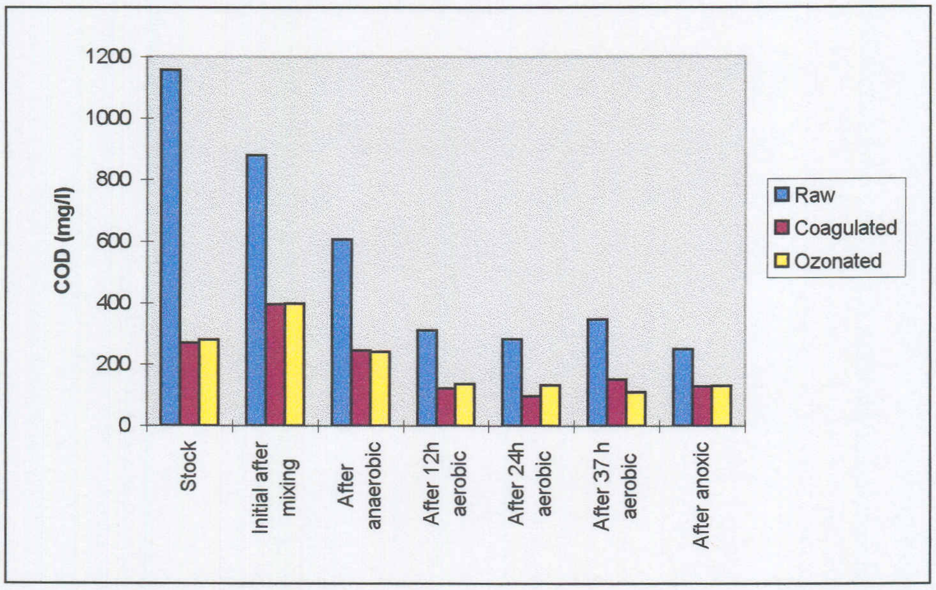

Figure 5.5 : COD reduction during Darvill activated sludge batch test.

The COD of the raw textile effluent decreased to a minimum of 282mg/l after 24 hours of aerobic treatment and then rose again to 346mg/l after 37 hours of aerobic treatment. The COD decreased to 250mg/l after the anoxic period. The COD of the coagulated effluent followed a similar trend, with a minimum COD of 97mg/l after 24 hours aerobic treatment, rising to 151mg/l after 37 hours of aerobic treatment and then falling to 127mg/l at the end of the anoxic period. The coagulated and ozonated textile effluent followed a slightly different trend by decreasing in COD throughout the aerobic period to a minimum COD of 110mg/l before increasing to 130mg/l during the anoxic period.

Summary of batch test results

The corrected colour results show that although colour removal from the raw effluent by both Hammarsdale and Darvill activated sludges was reasonable at approximately 55%, the colour actually increased for both the coagulated effluent and the coagulated and ozonated effluent, with the effect being more marked in the Darvill sludge batch test. This was intriguing as this plant receives little dyestuff and the sludge would thus contain little dye to desorb during the activated sludge process. It is interesting to note that in many cases the minimum colour was reached after 12 hours aerobic treatment and that the colour increased thereafter. This would suggest that the aerobic period should be reduced to 12 hours provided sufficient COD removal and nitrification could be achieved in the reduced period.

COD removal was good in the case of the raw effluent with an average of 77% removal based on the raw COD. The COD removal for both the coagulated and the coagulated and ozonated samples was also good with an average of 55% based on the coagulated, and coagulated and ozonated sample's initial COD. The majority of the COD reduction was achieved within 12 hours aerobic treatment, once again indicating the possibility of a shorter aerobic period.

Although the COD results of the two treated samples were essentially the same, showing that the ozonation does not appear to have increased the overall biodegradability of the effluent, the final colour of the ozonated sample remains lower than the sample which was simply coagulated. The colour difference between the ozonated and un-ozonated samples decreased a little during activated sludge treatment.

5.4. TERTIARY TREATMENT OF EFFLUENT - CONCLUSIONS

Using the initial OUR as an indicator of biodegradability, the coagulated and ozonated effluent showed the greatest biodegradability, followed by the coagulated and raw effluents. This is in agreement with the Judkin (1981).

The OUR data obtained from the Darvill activated sludge batch test showed a little biological inhibition with the raw effluent, and a hint of inhibition with the coagulated, ozonated effluent.

Although the activated sludge batch tests removed approximately 55% of the colour from the raw effluent, no colour was removed from the coagulated, and coagulated and ozonated, samples. This latter colour removal performance corresponds with research performed by Grau (1991), which showed that even with combined treatment of textile effluent, the final effluent was often coloured. The batch tests showed that the minimum colour was achieved within 12 hours which indicates that a reduction in the aerobic period may be possible.

COD removal was good in all cases with 77% removal for the raw effluent and an average of 55% removal for the samples which had undergone pre-treatment. The majority of the COD removal took place within 12 hours.

CHAPTER 6 : CONCLUSIONS

6.1. CONCLUSIONS

The conclusions reached in this investigation are set out below under separate headings according to the treatment stage.

6.1.1. PRIMARY TREATMENT

Ferric chloride was found to be the most effective coagulant, using a lower dose than alum. Polymeric coagulant blends provided by two suppliers were not successful.

Colour removal with ferric chloride was optimised using enhanced coagulation which entailed lowering the pH to 5 before adding 200mg/l ferric chloride under rapid mixing. Floc formation and sludge volume were optimised by adding 1.5mg/l R150 polyacrylamide. The adjustment of the pH back to 6.5 before removal of the sludge was found to adversely affect colour removal.

The optimum rapid mixing time for the ferric chloride was found to be 60s, while the optimum rapid mixing time for the R150 was found to be 30s. No slow mix was required.

Colour removal in excess of 70% was achieved using ferric chloride optimised as described above.

6.1.2. SECONDARY TREATMENT

Oxidation of the coagulated textile effluent with chlorine and hydrogen peroxide at doses of up to 20mg/l and 50mg/l, respectively, were unsuccessful.

Oxidation with ozone and peroxone produced almost identical results indicating no advantage in using peroxone. An ozone dose of 30mg/l at neutral pH produced a 48% reduction in colour and changed the hue from a green/brown to orange.

6.1.3. TERTIARY TREATMENT

The activated sludge batch test using an un-acclimated sludge showed some inhibition of metabolism with the raw textile effluent. No inhibition was observed in the case of the coagulated textile effluent, while there may have been a little inhibition in the case of the ozonated sample. The highest initial OUR was observed for the ozonated sample, and the lowest for the raw sample.

The analytical results, corrected for background colour and COD in the RAS, showed that although the COD remains approximately constant after the initial 12 hours of aeration, the colour reaches a minimum at 12 hours and then tends to increase once again. This indicates that the long period of aeration may be able to be reduced down to 12 hours without a negative effect. The colour increase was experienced with both sludges, precluding the possibility of desorption of colour absorbed prior to the batch test, from the highly coloured Hammarsdale sludge.

Using ozonated samples, colour removals of 30% and 32% were obtained after 12 hours aerobic treatment with the Hammarsdale and Darvill sludges respectively, giving colours of 58°H and 45°H. The COD results for the same sample at the same stage of treatment show a reduction of approximately 49% with values of 143mg/l and 137mg/l respectively.

6.1.4. GENERAL

It can be concluded that the primary and secondary treatments discussed above can remove a substantial amount of the colour and COD from the textile effluent before discharge to the sewer. Depending on the trade effluent tariff structure in use, a large saving in charges could be achieved, with an approximate treatment cost of R0-38/m^3 for coagulation and flocculation alone, increasing to R0-46/m^3 with ozonation.

The research also shows that the pre-treated effluent is less toxic to the activated sludge, and will produce a less coloured final effluent.

6.2. NEED FOR FURTHER RESEARCH

The results for the primary and secondary treatment investigations are considered to be fairly conclusive, but further research is needed into the optimisation of colour removal by means of activated sludge.

To this end a comprehensive pilot plant study needs to be conducted using pre-treated effluent to investigate the colour removal capability of the activated sludge system as it is presently configured, and then to carry out an optimisation of the system by varying the anaerobic, aerobic, and anoxic periods. This investigation would also need to monitor other factors such as phosphate removal, nitrification, de-nitrification and settling.

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APPENDIX 1

Table A.1 : Works influent analysis (1998).

Determinand	Units	n	Mean	Median	Miniumum	Maximum
pH		52		7.6	5.2	11.6
Colour	°H	**				
Conductivity	mS/m	52	194	196	58	343
Alkalinity	mg/l as $CaCO_3$	52	241	218	71	667
Total phosphate	mgP/l	52	7364	6705	1290	17430
Soluble phosphate	mgP/l	52	4037	3560	50	11480
Suspended solids	mg/l	52	3101	204	44	1435
COD	mgO_2/l	52	1472	1234	506	3766
TKN	mgN/l	52	62	50	11	158

** Not analysed due to turbidity interference.

Table A.2 : Works effluent analysis (1998).

Determinand	Units	n	Mean	Median	Miniumum	Maximum
pH		50		7.5	7.1	7.9
Colour	°H	48	91	86	16	354
Conductivity	mS/m	108	224	231	71	344
Alkalinity	mg/l as $CaCO_3$	49	150	144	49	334
Nitrate	mgN/l	49	0.5	0.5	.3	2
Ammonia	mgN/l	49	5	4	0.7	28
Total phosphate	mgP/l	49	614	550	250	2400
Soluble phosphate	mgP/l	49	293	230	50	1410
Suspended solids	mg/l	49	11	10	2	19
COD	mgO_2/l	49	70	70	10	108
TKN	mgN/l	48	7	6	2	29

Table A.3 : Textile mill effluent analysis (1998).

Determinand	Units	n	Mean	Median	Miniumum	Maximum
pH		45		7.2	3.2	10.2
Colour	°H	45	543	395	11	1880
Conductivity	mS/m	45	418	373	20	1365
Alkalinity	mg/l as $CaCO_3$	11	436	254	5	1546
Total phosphate	mgP/l	11	1127	1080	250	2300
Soluble phosphate	mgP/l	11	207	210	50	490
Suspended solids	mg/l	11	129	60	28	802
COD	mgO_2/l	45	1542	1502	201	3197
TKN	mgN/l	11	48	43	10	95

COAGULANT WORKING SOLUTIONS

Working solutions were made up as follows:

- Alum - 17.3913g stock alum (46%m/m, SG = 1.31) was diluted to 100ml using ultrapure water to produce a solution where 1ml≡80mg alum.
- Ferric chloride - 18.6047g stock ferric chloride (43% m/m) was diluted to 100ml using ultrapure water to produce a solution where 1ml≡80mg ferric chloride.
- R150 polyacrylamide (Floccotan, PO Box 1818, Pietermaritzburg, 3200) - 0.16g R150 was weighed into a beaker. 5ml alcohol was added under stirring to wet the polyacrylamide crystals. 95ml of ultrapure water was then added and the solution left to stir for at least half an hour before use. This produced a solution where 1ml≡1.6mg polymeric coagulant.

GENERAL COAGULATION METHOD

Titration Curve

In order to be able to adjust the pH of the effluent accurately to ensure that the final pH after coagulant dosing could be predicted to within a small (0.1) pH range, it was necessary to produce a pH titration curve by titrating an 800ml effluent sample with 1M HCl. In addition to this the pH reduction produced by the coagulant addition was also determined and converted to an equivalent volume of 1M HCl which was then subtracted from the acid volumes for pH correction purposes.

The pH titration curve is shown below.

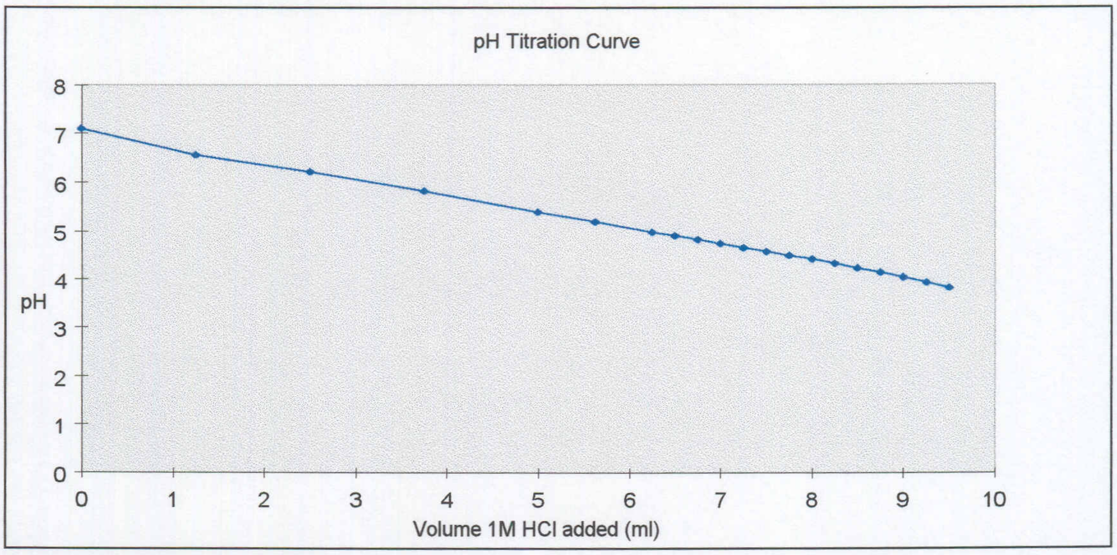

Figure A.1 : Titration curve for textile effluent.

The 1M HCl equivalent volume of the 2ml ferric chloride solution added to the dyehouse effluent was calculated as follows:

pH reduction of 2mls of $FeCl_3$ solution = 7.17 - 5.87 = 1.3
pH reduction for 1M HCl = 0.432 pH/ml
= 0.1 pH units/ 0.231ml

Volume 1M HCl equivalent to 2ml $FeCl_3$ solution = 3.01 ml

This volume was then deducted from the volume of the acid calculated to be necessary to lower the pH to the desired value.

Coagulation

Coagulant was added to 800ml effluent samples which underwent a rapid stir at 300rpm for 2 minutes and then a slow stir at 40 rpm for a further 15 minutes. The sample was then carefully poured into an Imhoff cone and allowed to settle for 30 minutes. The Imhoff cone was then tapped a couple of times and the sludge allowed to settle for a further 15 minutes before reading the sludge volume. Samples of the supernatatant were decanted for analysis.

ANALYSIS

All analyses were performed using Umgeni Water methods as accredited by the SABS. Summary descriptions of the methods are given below:

- pH - ion selective electrode.
- Conductivity - platinum electrode conductivity cell.
- Colour - spectrophotometeric measurement of absorption at 400nm after pH adjustment of samples to a common pH of 7 and filtering through a 0.45μm filter to remove suspended solids.
- COD - closed reflux microwave method (Slatter and Alborough, 1990).
- THM's - aqueous injection gas chromatographic method using internal standard and electron capture detector.