RENOVATION OF WASTEWATER FOR DIRECT RE-USE IN AN ABATTOIR

by

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Abstract

Tertiary treatment methods were tested on secondary effluent from an abattoir biological wastewater treatment plant with the purpose of renovating it for re-use in the abattoir. The colour and dissolved organic matter could be removed to such an extent that the water would comply with water of *insignificant health risk* (Department of Health). The treatment process sequence proven to be effective in upgrading this water to *insignificant health risk* standard were coagulation with a polymer blend, separation, ozonation, filtration and activated carbon filtration. The development of biologically activated carbon in practice was accepted as inevitable and desirable for optimum water quality, but not tested. A deciding factor in the selection of an appropriate treatment was that the final water would also have acceptable corrosion properties.

Keywords

Abattoir, recycle, secondary effluent, humic acids, colour, coagulation, ozonation, activated carbon, biologically activated carbon

Uittreksel

Tersiêre behandelingsmetodes op sekondêre uitvloeisel vanaf 'n biologiese suiweringsaanleg op 'n abattoir is getoets vir die moontlikheid om hierdie water op te gradeer vir hergebruik in die abattoir. Die water kon gesuiwer word om te voldoen aan waterkwaliteit met 'n *onbeduidende gesondheidsrisiko* (Departement van Gesondheid). Die proses volgorde wat gebruik was is koagulasie met 'n polimeer produk, skeiding deur sedimentasie, ozonering, filtrasie en adsorpsie met geaktiveerde koolstof. Die ontwikkeling van biologiese geaktiveerde koolstof word verwag indien die proses op volskaal gebruik word en was in aanmerking gebring in die finale aanbeveling.

Die korrosiwiteit van die gesuiwerde water was ‘n belangrike faktor in die keuse van die finale proses stappe.

Sleutelwoorde:
Abattoir, hergebruik,sekondêre uitvloeisel, humus sure, kleur, koagulasie, ozonering, geaktiveerde koolstof, biologiese geaktiveerde koolstof.

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1. INTRODUCTION

Water has always been a scarce resource in South Africa (Die Departement van Waterwese, 1984). The demand for fresh water supplies by the turn of the century would exceed the maximum water delivery predicted by the current runoff and rainfall patterns. Population growth predictions in the Gauteng Province (Schutte and Pretorius, 1995) indicate that this shortage would become critical in this region. The cost of water is set to increase significantly (Pretorius *et al*., 1995) as more strain is put on present water supply systems and new sources developed. Statutory water restrictions and the financial implications will force industries to investigate ways of reducing their fresh water demand.

Water demand can be reduced by optimising the use of water in the industry and by renovating and re-using the effluent (Funke, 1969). Industries with a low consumptive water use (Cowan and Steenveld, 1990) such as abattoirs, could benefit most from implementing such strategies. The Johannesburg Abattoir has already reduced their water demand by optimising the use. This done, the volume of effluent generated is still more than half of the fresh water demand. This effluent is treated with a protein recovery biological treatment system (Pretorius *et al*., 1995). It could be renovated for re-use to replace part of the daily fresh water intake.

The technology for water renovation for re-use of biologically treated effluents is well established in South Africa (Taljard, 1981) and was successfully implemented by the City of Windhoek, Namibia. Tertiary treatment processes such a coagulation, filtration, oxidation, activated carbon adsorption, membrane processes, chemical stabilisation and disinfection are commonly found (Van Vuuren and Taljard, 1979) as part of such renovation plants.

The purpose of this research was to evaluate tertiary treatment processes for effectiveness in renovating the secondary effluent from an abattoir single cell protein recovery effluent plant to a quality that can be re-used in part of that abattoir. The final water quality should conform to health, aesthetic and economic criteria for the designated use (Pretorius *et al*., 1995).

2. LITERATURE SURVEY

This survey covers the expected quantity and quality of secondary effluent from Johannesburg Abattoir available for re-use, the required quantity and quality and the treatment methods that could be used to purify the secondary effluent to this quality.

Abattoir water balance

Optimisation of water usage's in the Johannesburg abattoir has led to a reduction in water demand from 3.5 m^3/head to 1 m^3/head (Pretorius, 1996). The average total water demand of the abattoir is currently 2000 m^3/day. Surveys (Figure 2, appendix 1 (Van Heerden, 1995)) have shown that around 1500 m^3/day of secondary effluent is available for re-use.

The water demand for use in lairage washdown, offal washing and by-product manufacturing (PPF main) averages around 1250 m^3/day (Figure 3, appendix 1). This water does not come into contact with products intended for human consumption. The quality of water required in these processes need not be of general drinking water standard (Cowan and Steenveld, 1990). Part of the 1500 m^3 renovated secondary effluent could be re-used to supply this demand.

Required water quality

In an abattoir, water of drinking quality is required for all processes that bring it into contact with products for human consumption. This excludes areas of lairage washdown, cooling and refrigeration, general washing, vehicle washing and yard washing and gardening (Cowan and Steenveld, 1990). This "second grade" water should still be of good enough quality not to adversely affect health (1), be aesthetically acceptable (2) and not have an adverse impact on economics (3) (Funke, 1969).

1. The water should not be unhygienic or promote unhygienic conditions. The Director of Meat Hygiene, or any person he may delegate, is empowered to prevent the use of water in an abattoir if he suspects that water is "impure, unhygienic or not fit for its purpose" (Abattoir Hygiene Act, 1992). Table 1 in Appendix 1 represents proposed drinking water

guidelines considered for application in South Africa by the Department of National Health (Pieterse, 1989). Water of an insignificant health risk quality is acceptable for supply as drinking water for limited periods and should be suitable for the "second grade" water in the abattoir.

2. Water should be free from material that will settle to form objectionable sludge deposits, free from floating materials, oil and scum and other floating materials and also free from materials causing colour and odour to such a degree as to cause a nuisance (Krenkel and Novotny, 1980). Odour could change taste and smell (Meiring and Cohen, 1981) of food products.

3. The prevention of deposits and bacterial growths in pipes, containers and process kettles (Cowan and Steenveld, 1990) is necessary to prevent unnecessary maintenance. Corrosion and aggression would lead to failure of heat exchangers and conduits and increase in maintenance (Funke, 1969).

Expected quality of secondary effluent

Secondary effluents from industrial and domestic biological wastewater treatment plants are generally not suitable for direct re-use. Although most of the organic matter should be removed (90-95% in the abattoir) these effluents still contain micro-organisms, some suspended material and dissolved organic matter (DOM) which (Manka *et al.*, 1974) can cause colour, taste and odour.

The DOM in secondary effluent from biological treatment of domestic and industrial wastewater would be similar (Rebhun *et al.*, 1969; Narkis and Rebhun, 1983) to that in highly coloured surface water. About 45% of DOM in secondary effluents are humic matter (Manka *et al.*,1974) where this percentage is approximately 50% (Sierka *et al.*, 1989) in coloured surface waters. Humic matter is formed by biological degradation processes (Boero *et al.*, 1996). It consists mainly of anionic, highly unsaturated macromolecules (Christman and Ghassemi, 1966).

Organic matter in secondary effluents would increase disinfectant demand (Rogers *et al*., 1987) and decrease disinfection efficiency (El-Rehaili and Weber . r, 1987). It will also lead to the formation of disinfectant by-products (Vik *et al*., 1985). The organic matter would also be the cause of objectionable colour and odour in the secondary effluent (Sierka *et al*., 1989). It may cause bacterial growth in the distribution systems and equipment that can cause obstruction and other undesirable effects on the process (Krenkel and Novotny, 1980). For these reasons the DOM and specifically the humic matter (Constantine, 1982), has been identified as priority pollutants in drinking water purification (Rogers *et al*., 1987).

Tertiary treatment for re-use

The removal of humic matter as the primary constituent of DOM has been identified as a priority in drinking water purification (Grozes *et al*., 1995) and in wastewater treatment for re-use (Rogers *et al*.,1987). Processes used for removal of humic matter from coloured surface water has been extensively researched and includes coagulation, oxidation, activated carbon adsorption and membrane processes such as reverse osmosis and ultra- and nanofiltration (Taljard, 1981) and combinations of these.

Conventional treatment (Fettig and Ratnaweera, 1993) for humic matter (colour) removal would involve coagulation with alum or ferric chloride, stabilisation and disinfection. Ozonation followed by biologically activated filtration (with either activated carbon or sand as medium) and disinfection has been proved (Juby and Botha, 1994) to be an effective alternative. The capital and operating cost (Constantine, 1982) is equal or less than required with conventional treatment with reduced sludge disposal and filter maintenance. Latest research (Juby and Botha, 1994) has found membrane processes still less economical than either of the previous two processes mentioned.

Coagulation

Coagulation is the process that removes pollutants from water by chemical addition, rapid mixing and flocculation. The mechanisms for humic matter removal would be charge neutralisation by precipitation or by co-precipitation with the coagulant. Humic matter could also adsorb on the surface of an aluminium- or ferric hydroxide precipitate (Jacangelo *et al*., 1995).

Characterisation of organics functional groups can provide insight into the type of coagulant and conditions that would be effective in organic matter removal (Owen *et al.*, 1995). Humic matter consists of negatively charged macromolecules (Semmens and Field, 1980) with the degree of ionisation or charge density depending on pH (Grozes *et al.*,1995). A higher charge density at high pH would result in molecules which are difficult to chemically coagulate by charge neutralisation and also less easily adsorbed (Kuo and Amy, 1988).

When a metal salt like ferric chloride or alum is added to water, a series of polymeric hydrolysis intermediates is rapidly formed (Hong-Xiao and Stumm, 1987) before aluminium- or ferric tri-hydroxide precipitates. Semmens and Field (1980) and Edwards and Amirtharajah (1985) concluded that these intermediate species actually complexes and precipitate humic matter. The charge densities of these intermediates are influenced by pH (Grozes *et al.*, 1995) and increase at low pH.

Commercially prepared polymers of aluminium or iron like poly-aluminium chloride (PACl) would have the same charge neutralisation effect as the hydrolysis intermediates. Their reaction rate (Dempsey *et al.*, 1985) may be faster since the polymerisation step is bypassed. Organic poly-electrolytes are often used in conjunction with metal salts for added complexing and bridging ability (Mortimer, 1991). The charge densities (Scheuch and Edzwald, 1981) on PACl and organic poly-electrolytes are controlled by the manufacturing process and they are often synthesised with a charge separation that is higher than found on the hydrolysis intermediates. The total coagulant demand in joint systems is often lower than the sum of half of each coagulant on its own (Edwards *et al.*, 1994). Blends between poly-amine and PACl attempt to take advantage of this fact. Kerdachi *et al.* (1994) found very good removal of humic matter with such a product.

When choosing a poly-electrolyte for coagulation of humic matter, it is useful to be aware of the different classes and characteristics of polymers that are available. Poly-metal electrolytes like aluminium chloride is generally formulated as $Al_n(OH)_mCl_{3n-m}$ (Viraraghavan and Wimmer, 1988) or similar ferric polymers. Organic poly-electrolytes can be divided into coagulants and coagulant aids for water treatment. Coagulants generally fall in a molecular weight range of 50000 g/mol and can be natural tannins or synthetic branched or straight chains of poly-amine (Mallevaille *et al.*, 1984). Coagulant aids are generally synthetic polymers with acrylate as monomer. They fall in the molecular weight range of > 1000000 g/mol. These can be grouped according to charge distribution into cationic, non-ionic and anionic polymers. Anionic and non-ionic poly-acrylamides are used as flocculant aids with coagulants such as metal salts or poly-amines. Cationic poly-acrylamides are generally used as sludge conditioning and dewatering aids (Carns and Parker, 1985). They are sometimes used as primary coagulants in wastewater with a very high solids content.

The more hydrophilic fraction of organic matter (low molecular weight, high charge) may not be removed by precipitation with any polymers, but can be removed by adsorption on a metal hydroxide precipitate (Edwards *et al.*, 1994). Organic matter with a high hydrophilic component (Yao and O'Melia, 1989) may be more effectively coagulated with metal salts. Oxidation could potentially increase the low molecular weight fraction of humic matter while increasing the polarity and acidity of the fraction at the same time and could make it less amenable to removal by coagulation (Owen *et al.*, 1995).

Colour as indicator of organic matter

The nature of colour in biological wastewater is often organic (Black and Willems, 1961) and caused by humic-, fulvic- and hymathomelanic acids (Sierka *et al.*, 1989). The basic structure of humic matter is a chain built up with phenolic nuclei (Christman and Ghassemi, 1966). The chain is characterised by alternating double and single bonds that are termed chromophores (Rice and Bollyky, 1981). These absorb UV and visible light, causing colour. UV absorbance at 254 nm is normally used to measure humic matter (Sierka *et al.*, 1989). Colour measurements and UV absorbance correlated (Vik *et al.*, 1985) with coefficients varying between 0.93 and 0.97.

In practice, coagulant dose on a plant is often determined by colour intensity (Johnson and Amirtharajah, 1983). Removal of organic matter by adsorption can also be monitored using colour (Van Breemen *et al.*, 1979) as long as the ratio between the colour causing and other DOM is known. When establishing the efficiency of these two processes for removal of DOM, only colour removal could be monitored.

Oxidation would attack double bonds and reduce conjugation (Eaton, 1995), thereby reducing colour and UV absorbance. Humic acids are oxidised into simpler acids (Constantine, 1982) but not removed. Colour cannot be used as an indicator for organic matter removal when oxidation is used.

Ozonation for colour removal

The reduction in the ultraviolet absorbance and colour of water containing organic compounds when samples are ozonated is caused (Sierka *et al.*, 1989) by the oxidation of unsaturated structures. The conjugation responsible for colour and UV absorbance is removed (Rice and Bollyky, 1981). Water containing 525 mg/l humic acids tested by (Symons, 1980) required 100 mg/l ozone to destroy 95% of the colour. About 4-5 mg/l Pt-Co (1 mg/l Pt-Co = 1 hazen) are removed per 1 mg/l ozone but reduction is normally non-linear (Tan and Amy, 1991) with significant reductions at low ozone dosages with a refractory fraction remaining. Colour removal was enhanced with longer retention times (Juby and Botha, 1994).

When ozone is added to water it decompose as follows:

$O_3 + H_2O \rightarrow HO_3^- + OH^-$

$HO_3^- + OH^- \rightarrow 2HO_2\cdot$

$O_3 + 2HO_2\cdot \rightarrow HO\cdot + O_2$

$HO\cdot + HO_2\cdot \rightarrow H_2O + O_2$

The $HO\cdot$ and $HO_2\cdot$ radicals are very reactive (McCarthy and Smith, 1974) but not very selective oxidants while molecular ozone reacts more specifically and is reactive towards high molecular weight organics. The products of reaction of molecular ozone with double bonds are olefin ozonides (Razumovski and Zaikov, 1984) which would decay into bipolar ion and carbonyl compound such as aldehydes and ketones. The reaction products of unsaturated organics with radicals (Goel *et al.*, 1995) are alcohols and carboxylic acids. Humic acids are normally oxidised to acetic, formic and oxalic acids (Edwards and Benjamin, 1992), therefore the reaction mechanism is probably with the radicals. Radical attack would predominate at low ozone dosages, high pH and on less aromatic organics.

These products of the reaction between humic matter and ozone would be more biodegradable than the humic matter. This is confirmed by Millamena (1992) who observed a decrease in chemical oxygen demand (COD) of a sample of water containing humic acids and increase in biological oxygen demand (BOD) while the total organic carbon (TOC) stayed constant. Bacterial regrowth is likely (Symons, 1980) if ozonation is used as a terminal step in a water treatment programme. Increase in biodegradability is, however, an advantage when biologically activated carbon is used (Constantine, 1982) to reduce organic matter after ozonation (McCarthy and Smith, 1974).

Low ozone dosage on water containing organics and turbidity sometimes improved removal of turbidity through filters (Rice and Bollyky, 1981) and decrease coagulant demand. DOM adsorb onto particle surfaces and increase surface charge and electrophoretic mobility and stability of the particle. Ozonation could lead to the desorption of the organic matter because of oxidation of the latter, therefore destabilising the colloid (Chang and Singer, 1991). Ozonation could also lead to the formation of metastable organic polymers from the DOM and lyse algal cells, releasing biopolymers, both of which can act as bridges between particles and improve coagulation (Grasso and Weber, 1988). Ozone can neutralise negative colloids and turbidity can be oxidised and neutralised (McCarthy and Smith, 1974).

Ozone could also decrease removal of turbidity due to the formation of low molecular weight more oxygenated compounds like carboxylic acids (Grasso and Weber, 1988) which can complex with metal ions and keep them in solution. Higher ozone dosages (Chang and Singer, 1991) as well as suboptimal dosages can increase turbidity in final water (Rice and Bollyky, 1981).

Activated carbon adsorption

Activated carbon adsorption is widely used in wastewater treatment, especially in industry where coloured organic pollutants such as dyes and hazardous organic matter needs to be removed (Albanese *et al.*, 1981). It can be used in both powdered (95-100% pass through a 100-mesh sieve) and granular form, graded according to size (Weber, 1984). Different types of granular activated carbon may perform differently with respect to adsorption capacity of a system (Benefield *et al.*, 1982; Weber, 1984). The pore size distribution of the activated carbon will impact on the effectiveness of DOM removal since this will influence penetration of the larger organic matter (El-Rehaili and Weber Jr, 1987).

A reasonable understanding of the adsorption mechanics of trihalomethanes (THM) by activated carbon exists, but less is known of the adsorption behaviour of humic substances (Weber Jr *et al.*, 1981). Most experiments to obtain adsorption and similar data is conducted on analytical grade humic acid of known composition. The variability of humic acids in nature limits the applicability of this data to complex systems.

Particles of low molecular weight and polar nature are generally not adsorbed well, while high molecular weight less polar organics like aromatic and substituted aromatic species are generally strongly adsorbed (Weber, 1984). Ozone would tend to convert low polarity aromatic compounds to polar aliphatic compounds (Van Leeuwen *et al.*, 1981) which would not be as well adsorbed by activated carbon as the less polar humic matter (Rogers *et al.*, 1987).

The equilibrium capacity of carbon for uptake of a compound as well as the rate of approach to equilibrium must be known and can be determined by batch adsorption tests (Crittenden and Weber, 1978). In order to design a fix-bed adsorber, the shape of the breakthrough curve and the time of breakpoint must be estimated as well. These breakthrough curves would be specific to a particular application (Weber, 1984).

Reactivation of activated carbon is normally conducted by adding controlled quantities of water to an oxidant atmosphere. About 11 kJ/kg of carbon is consumed for reactivation, but burning of the off-gas consumes about 5000 kJ/kg of carbon (Masschelein, 1992).

Biologically Activated Carbon

Catalytic and biological degradation of DOM can take place in granular activated carbon adsorption columns (Weber Jr *et al.*, 1981). The surfaces of the carbon provide very good colonisation sites that are sheltered from shear forces (Van Leeuwen *et al.*, 1981) and the adsorptive properties of the carbon lead to substrate and oxygen enrichment on the carbon surfaces (Qi *et al.*, 1992). The deliberate use of bacterial growths on granular activated carbon to DOM from water has been studied as a process and is termed biologically activated carbon (BAC) (Van Leeuwen *et al.*, 1981).

BAC is often enhanced by pre-ozonation (Millamena, 1992) because of the increase in biodegradability of most organic water soluble polymers (Dowbiggin and Singer, 1989). The water would be enriched with oxygen which further promotes growth (Van Leeuwen *et al.*, 1981). The ozone dose necessary to improve biodegradability of humic matter was found to be 1-2 mg/mg TOC (Juby and Botha, 1994).

It was found with pre-ozonation of water containing humic matter that it takes about 2 months for biological activated carbon to develop. A steady state was achieved without regenerations with removal of 59% (Rogers *et al.*, 1987) to 60% (Juby and Botha, 1994) of dissolved organics originating from humic and fulvic acids after ozonation. Bio-activity would depend on the C/N/P ratios in the water and temperature. Nutrient addition may be necessary for optimum operation of biologically activated carbon (Juby and Botha, 1994).

The carbon is effectively regenerated by the biological assimilation of pre-absorbed organic matter (Masschelein, 1992). Therefore, it is found that the periods between required physical regeneration of activated carbon can be prolonged for example from 70 days to 480 days (Netzer *et al.*, 1984).

Removal of micro-organisms

Coagulation and Flocculation

Results from coagulation studies on raw effluent from abattoirs suggest that a better removal of micro-organisms is obtained at low pH (De Zutter and Van Hoof, 1981). Primary lime clarification seems to be more effective in the removal of micro-organisms than coagulation with other coagulants due to the biocidal effect of high pH.

Ozonation

The first application for ozone treatment of water had disinfection as its objective. Ozone has proved very efficient in removal of viruses and parasites as well as bacteria (Masschelein, 1992). The concentration-time (CT) concept is normally the principle for applying ozone by the EPA in the USA, but this factor normally includes the chemical ozone demand of a specific water.
The ozone demand of a water needs to be met first before any disinfection with ozone can take place (Rice and Bollyky, 1981). Adequate disinfection can be obtained with ozone residuals of 0.5 to 1.5 mg/l after the demand has been met. For the same bacterial kill, water with a COD of 74 mg/l needed a dosage of 3 times that needed for water with a COD of 30 mg/l. Ozone demand does not follow a breakpoint demand pattern and is influenced by the value of the residual (National Institute for Water Research, 1981). Ozone demand in secondary effluent would consist of matter that is readily oxidised by ozone such as humic matter (Venosa and Meckes, 1983). The high dosages needed to obtain the CT values required for adequate disinfection may be detrimental for other purification processes like flocculation and increase in biodegradability (Wilczak *et al.*, 1992). Ozone would not be a cost effective disinfectant in high ozone demand waters.

Adsorption on activated carbon

Micro-organisms may attach to an activated carbon column to form biologically activated carbon (Masschelein, 1992). However, activated carbon columns often have large interspatial areas and are not good filters for colloidal matter (Benefield *et al.*, 1982). If biologically activated carbon develops the micro-organism count in the final water may increase due to organisms periodically being washed off the carbon (Masschelein, 1992).

Terminal disinfection with chlorine

When chlorine is used as a disinfectant, it should be ensured that enough of the active disinfecting species is maintained for the desired contact time to achieve bacterial kill (White, 1992). The type of chlorine residual being measured should be established, since products like chloramines contain available chlorine and can be measured as residuals

Organic impurities and nitrogen compounds in water destroy the active chlorine by substitution to form chlorinated organics and chloramines (American Public Health Association *et al.*, 1991). This constitutes the chlorine demand. The chlorine demand of a water can be defined as the difference between the added chlorine dose and the residual chlorine concentration, measured after a prescribed contact time at a given time and temperature. Coagulation and ozonation are often used to reduce chlorine demand by removing and oxidising organics and ammonia nitrogen (Krasner *et al.*, 1989).

Chlorine reacts with ammonia-nitrogen in water to form mono-, dichloramine and nitrogen trichloride, which can be measured as combined residual chlorine. The reaction of increasing chlorine dosages with the ammonia in water to form these species produce the breakpoint phenomenon (White, 1992). The reaction of chlorine with ammonia will proceed with increasing chlorine dose from the formation of monochloramine, to dichloramine and nitrogen trichloride until free nitrogen is formed. Until this point (the breakpoint), most of the total chlorine residual measured would be mono- or dichloramines. From this point, with increasing chlorine dose, free residual chlorine will appear and increase in the water.

Free residual chlorination as a process is commonly used as a disinfection regime to produce drinking water since it provides water with low taste and odour (White, 1992). In the free residual process, sufficient chlorine is provided to destroy all ammonia nitrogen present (the breakpoint). This destruction occurs at a ratio of chlorine to ammonia nitrogen of 10:1 by weight.

Chloramination can also be practised to maintain a chlorine residual for longer and prevent trihalomethane formation. Chloramines require longer contact times for similar bacterial kills than free residual chlorine (HOCl). Chloramination plants normally operate at a chlorine to ammonia nitrogen ration of 3:1 by weight (Krasner *et al.*, 1989). Chloramination is often practised when there is already ammonia present in the water, but can also be effected by adding ammonia when chlorinating (National Institute for Water Research, 1981).

Although chloramination can be employed as a disinfectant method, the most efficient disinfection will be obtained by free residual chlorination. For this process to be effective, the oxidation of ammonia-N to nitrogen gas at the breakpoint should be employed (White,1992).

Breakpoint chlorination for a water can be determined graphically by determining chlorine residuals at different contact times and plotting these against chlorine dose (Westrick and Cohen, 1976). The chlorine demand at any contact time would be the difference between the free available chlorine and the chlorine dose. Coagulation and ozonation could reduce demand and breakpoint by oxidising some matter that would have formed part of the demand (Ross *et al.*, 1976).

Chemical quality

Electrochemical reactions between water and metal components may give rise to dissolution of metal and precipitation of metal salts (Loewenthal *et al.*, 1986). Water can also accelerate galvanic corrosion between two dissimilar metals by increasing the electrical conductivity between the metals with a high dissolved solids content (Asano *et al.*, 1988). Aggressive water would dissolve away the cement matrix in asbestos cement and concrete conduits causing destruction of the integrity of the material (Benefield *et al.*,1982). An excess of calcium or magnesium ions in the water can precipitate to form scale. The presence of micro-organisms and DOM can cause bacterial build-up in pipes and equipment (Benefield *et al.*, 1982).

The principle of controlling aggression, corrosion and scale in water systems is by controlling the saturation of state of calcium carbonate in the water (Loewenthal *et al.*, 1986). The acidity and precipitation potential can be calculated by the Stasoft Computer programme designed by Loewenthal *et al.*, (1988). Regrowth of organisms can be prevented by minimising DOM and adequate disinfection (Funke, 1969).

Apart from these guidelines, a few other parameters need to be observed to control corrosion and aggression:

1. Water should have a sulphate content of less than 350 mg/l - otherwise the structure of cement should be altered (Loewenthal *et al.*, 1986).
2. The presence of DOM can cause a decrease in dissolution and precipitation rates of calcium carbonate and should be minimised (Loewenthal *et al.*, 1986).
3. Resultant alkalinity above 35 mg/l (Loewenthal *et al.*, 1986).
4. Limit TDS increase to prevent galvanic corrosion (Asano *et al.*, 1988).

5. Maintaining chloride and sulphate ions to below 50 mg/l each or maintaining the Larson-index $\frac{Cl^{-} + SO_4^{2-}}{Alkalinity}$ (Loewenthal *et al.*, 1986) to below 0.2 to prevent interference with passivation.

Lowering the pH to optimum for coagulation is easily done in waters of low alkalinity. Water with a high alkalinity would require high volumes of acid to reduce pH, adding chloride or sulphate ions to the water (Moyers and Wu, 1985). This increase will increase the Larson index. The use of a coagulant such as alum or ferric chloride may reduce pH. This is due to the consumption of hydroxide in forming metal hydrolysis intermediate species and trihydroxide precipitate during coagulation. About 0.5 mg/l alkalinity in the water is consumed for every 1 mg/l alum added (Ogedengbe, 1984). This is beneficial to the coagulation of colour, but the amount of coagulant required in high alkalinity waters will increase the chloride or sulphate concentration and the Larson index.

Objectives of this research

The secondary effluent from the Johannesburg Abattoir would be sampled on several selected days to establish the quality and variation. This would be compared with water quality for insignificant health risk in order to establish its suitability for re-use in the "second grade demand".

Coagulation would be examined for effectiveness of colour removal:

1. Different coagulants would be compared for colour removal against each other at varying dosage.
2. Appropriate dosages of the three best performing coagulants would be selected according to their impact on corrosivity and health criteria. These three would also be tested for effectiveness for turbidity removal.
3. These dosages would be used for comparing coagulants at different pH against each other.
4. The corrosivity would be determined for optimum pH and dosages to select the appropriate coagulation conditions

Ozonation would be evaluated before and after coagulation to establish:

1. Ozone demand

2. Ozone needed for colour removal.

Adsorption on activated carbon would be performed on coagulated and ozonated water to establish capacity for removal of colour.

Breakpoint chlorination would be performed to establish effect of purification steps on disinfection with chlorine.

The effective treatment sequence would be tested on a sample of secondary effluent and the results compared with water of insignificant health risk quality and corrosion parameters.

3. METHODS

Sample collection and testing

Twenty-five litre samples of secondary effluent from Johannesburg Abattoir were collected every second to third day during the experimental period. The samples were preserved at 4 °C between test runs, but allowed to reach ambient temperatures before any experiments were performed. The samples were shaken before aliquots for experimental procedures were drawn. Each sample of raw water was tested for total dissolved solids (TDS), chloride, sulphate, total alkalinity, total hardness, turbidity, colour, dissolved organic carbon (DOC), and total heterotrophic plate counts were performed.

Comparison of coagulants for colour removal

Initially a range of metal salt and poly-electrolyte coagulant blends were screened for their ability to remove colour. Of these, alum ($Al_2(SO_4)_3.18H_2O$), ferric chloride ($FeCl_3.6H_2O$) a Polyamine/poly aluminium chloride blend (hereafter refered to as PACl-blend) gave the best results. These were used for comparison of colour removal. Testing consisted of varying the chemical dosage without adjusting pH, and varying pH while keeping dosages constant as shown in Table 1. Metal ion concentrations is reported in mmol/l to compare reaction sites available.

Table 1: Determination of best coagulant for colour removal

Coagulant	Dosage	Metal ion	Counter ion	pH
Varying dosage				
Alum	30 - 400	0.1 - 1.8 mmol/l	13 - 173 mg/l SO_4^{2-}	7.6
Ferric	30- 400 mg/l	0.11 - 2,2	12 - 157 mg/l Cl^-	7.6
PACl-blend	30 - 120			7.6
Varying pH				
Alum	100 mg/l	0.3 mmol/l	43 mg/l SO_4^{2-}	4 - 7.6
Ferric	120 mg/l	0.4 mmol/l	47 mg/l Cl^-	4 - 7.6
PACl-blend	60 mg/l			4 - 7.6

For the varying pH testing, pH was adjusted with 5 N H_2SO_4 or 0.25 N NaOH solutions prior to coagulant addition and recorded after flocculation. Loewenthal *et al.*(1986) advised that the individual concentrations of chloride and sulphate concentrations should not exceed 50 mg/l each to limit corrosion. The counter ion contribution is noted in Table 1. Products containing polyamine generally have health limitations for use in drinking water (Mallevaille, *et al.*, 1984).

Comparing the colour removal at varying pH were therefore limited to:
100 mg/l $Al_2(SO_4)_3.18H_2O$.
120 mg/l $FeCl_3.6H_2O$.
60 mg/l PACl-blend - health limitation of 66 mg/l.

To identify the coagulant that gave consistently the best results for colour and turbidity removal at these dosages, the mean and standard deviation (Wine, R.L., 1964) was calculated for percentage removal obtained at constant pH for alum, ferric chloride and PACl-blend.

Coagulation were performed with the jar test method as recommended by Dental *et al.*(1988) and Lai *et al.* (1975). The best results were obtained by rapid mixing for 2 minutes at 295 rpm (G-value of $199.5s^{-1}$) after coagulant addition, followed by 20 minutes at 50 rpm (G-value of $12.6s^{-1}$) which was determined as the optimum mixing speed for colour removal (see Figure 5 in Appendix 2). 500 ml samples to 1 litre round glass beakers were used and the G-values were obtained using calibration of G in round beakers by Botha (1995). After 20 minutes settling, samples of supernatant was drawn for pH and colour measurement.

Chemical quality

Stabilisation dosage requirements were calculated for coagulant dosages and pH, using the Stasoft computer programme (Loewenthal *et al.*,1988). The corrosivity according to Larson: $\frac{Cl^- + SO_4^{2-}}{Alkalinity}$ were calculated using the theoretical alkalinity after stabilisation given by Stasoft. Loewenthal *et al.* (1986) recommended that this value should be less than 0.2.

Ozonation

Ozone was generated with a LN 103 ozone generator (Ozonia, Switzerland) with oxygen as a feed gas. The ozone generator was calibrated by bubbling ozone through a diffuser at the bottom of a 75 mm diameter contact column containing 1 litre of a 2% potassium iodide (KI) solution. Ozone dosage was varied according to the time of ozonation at constant voltage and gas flow. After each time period, the KI solution was transferred and titrated to a clear endpoint using 0.1 N sodium thiosulphate ($Na_2S_2O_3.5H_2O$) with starch as indicator as was described by Toerien, (1988) and Razumovski and Zaikov (1984), thereby measuring the amount of ozone transferred during each time interval. The ozone production rate was determined from these data.

The ozone demand of water (National Institute for Water Research, 1981) is defined as the amount of ozone consumed before a ozone residual is observed for a given time period. The readily oxidisable organic matter in water will deplete ozone (Venosa and Meckes, 1983; Rice and Bollyky, 1981) and constitute this demand. Since the unsaturated bonds on humic matter would be preferred sites for ozone attack, the demand would also represent the amount of ozone needed for colour removal (Grasso and Weber, 1988). Ozone demand was determined by applying ozone to distilled water and the sample at increasing dosages and measuring the ozone in the off-gas by trapping it in 2% KI and titrating with $Na_2S_2O_3$ (Toerien, 1988). The ozone absorbed by the sample and contact system would be the mass of ozone applied minus mass of ozone in off-gas per litre of sample.

The relationship between ozone absorbed and colour removal was determined by measuring the percentage colour removal with increasing applied ozone dose. Absorbed ozone was determined in the same manner as described for ozone demand.

Table 2 shows applied ozone dosages employed to obtain these relationships:

Table 2: Ozone combinations

Sample	Applied Ozone Dosage	Relationship
Distilled water	0 -80 mg/l	Reference curve
Secondary effluent	0 - 80 mg/l	Ozone demand curve
Flocculated Secondary effluent	0 - 60 mg/l	Ozone demand curve
Secondary Effluent	0 - 20 mg/l	Colour removal curve

Activated carbon adsorption

Activated carbon were added to treated secondary effluent water to compare the effect of ozonation on the removal of colour by adsorption. Amounts added is shown in Table 3.

Table 3: Activated carbon adsorption for colour removal

Sample	Activated Carbon Added
Flocculated Secondary effluent	50 -1000 mg/150 ml
Flocculated and Ozonated Secondary effluent	50 - 1000 mg/150 ml

Granular activated carbon type PHO 12/40 was supplied by Montan (Johannesburg) and added to 150 ml of sample and shaken for 12 hours before colour measurements were made.

Breakpoint chlorination

Breakpoint chlorination (White, 1992) was performed on secondary effluent and samples that were coagulated as well as samples that were coagulated and ozonated. Appropriate amounts of 300 mg/l sodium hypochlorite (NaOCl) solution were added to 50 ml samples and left for a contact time of 2 minutes. Additions were staggered in one minute intervals (American Public Health Association *et al.,* 1991). Total residual chlorine were determined in each sample after the contact time.

Comparison with guideline

The most effective treatment sequence was performed on a sample of secondary effluent. The product water quality after each treatment step was analysed for TDS, chloride, sulphate, alkalinity, hardness, pH, turbidity, colour and DOC. These were compared to the guidelines for health, aesthetic and economic criteria.

Analysis methods

- Organic matter removal with coagulation was measured by colour removal as was mentioned by Edwards and Amirtharajah (1985) and Van Breemen *et al.*(1979). This relationship between colour and COD removal was confirmed in this study (see Figure 3 in Appendix 2).

- COD was measured by the Merck Spectroquant photometer SQ 118 (E.Merck, Darmstadt)
- DOC was measured by the Rand Water Board Scientific Services.
- Samples were corrected to pH 7 and centrifuged before colour measurement (Crowther and Evans, 1981) with a Merck Spectroquant photometer SQ118 (E.Merck, Darmstadt), relating it to hazen units. TDS was determined gravimetrically on the centrifuged samples (American Public Health Association *et al.,* 1989).
- Samples were filtered through Whatman 4 filter papers before turbidity measurements. The nephelometric turbidity (Dental *et al.*,1988) was measured with a Hach turbidimeter model 2100 A (Hach,USA.).
- Total hardness was determined as in American Public Health Association *et al.* (1989) method no 2340C, alkalinity by method 2320, chloride with method 4500-Cl B, total heterotrophic plate counts with method 9215 B and total residual chlorine with method 4500-Cl F.

4. RESULTS

Sample Collection and Testing

The secondary effluent quality is compared to water of *no* and *insignificant health risk* in Table 4.

Table 4: Secondary effluent quality compared to requirements for water of *no* and *insignificant health risks*

Parameter	Secondary Effluent	*No health risk*	*Insignificant health risk*
TDS (mg/l)	664 - 1000	470	2000
Chloride (mg/l)	100 - 120	250	600
Sulphate (mg/l)	35	200	600
Total Hardness (mg/l as $CaCO_3$)	120	20-300	650
pH	7.65 - 7.8		5.5-9.3
Turbidity (NTU)	2.7 - 5.2 (29)	1	5
Colour (Hazen)	176 - 220	20	20
DOC (mg/l)	91	10	20
Total heterotrophic plate count (cfu/100ml)	2 X 10^6	<100	<1000

The TDS, chloride, sulphate, hardness and pH of the secondary effluent water were all within the limits of water quality of *insignificant health risk* (Pieterse, 1989). The chloride concentration is double the recommended 50 mg/l. The Larson index was calculated and averaged around 0.49, which is higher than the recommended 0.2 (Loewenthal *et al.*, 1986). The variation in turbidity was dependant on the operation of the secondary effluent plant and is illustrated in Figure 1, Appendix 1. Anaerobic conditions developed in the secondary clarifier over weekends and caused increase in turbidity up to 29 NTU. These conditions could be prevented by emptying the secondary clarifier over weekends

.

The colour, dissolved organic carbon (DOC) and microbiological quality (total heterotrophic plate count) of the secondary effluent did not comply with the requirement for water of *insignificant health risk*. These parameters were not influenced by anaerobic conditions in the clarifier.

Comparison of coagulants

Ferric chloride, alum, lime and a range of commercial coagulants from Ultrafloc, Floccotan and Zetachem were tested for colour removal. Figure 1 illustrates that ferric chloride, alum and Ultrafloc 3500 (U3500) performed the best for colour removal.

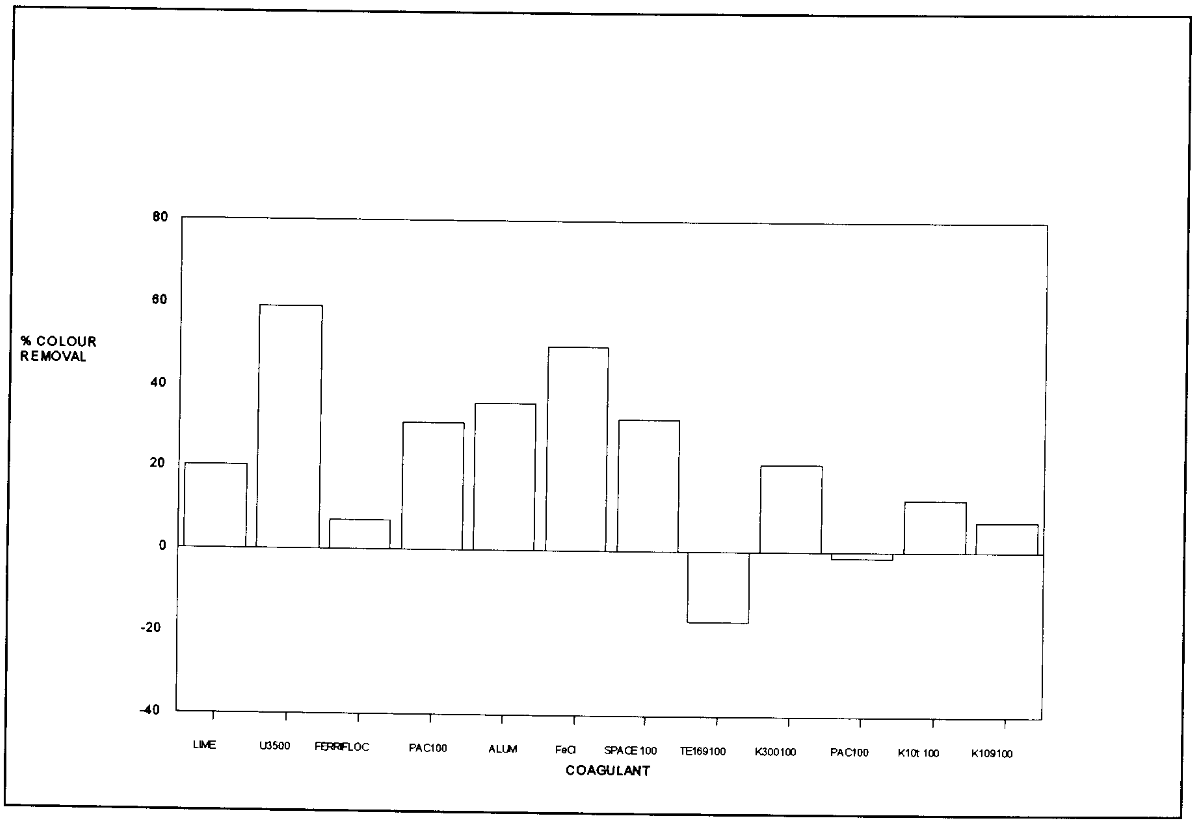

FIGURE 1: Comparison of different coagulants dosed at 100 mg/l for colour removal

Varying dosage

The effectiveness of alum, ferric chloride and U3500 for coagulating and removing colour is compared in Figure 2. No adjustments for pH were made.

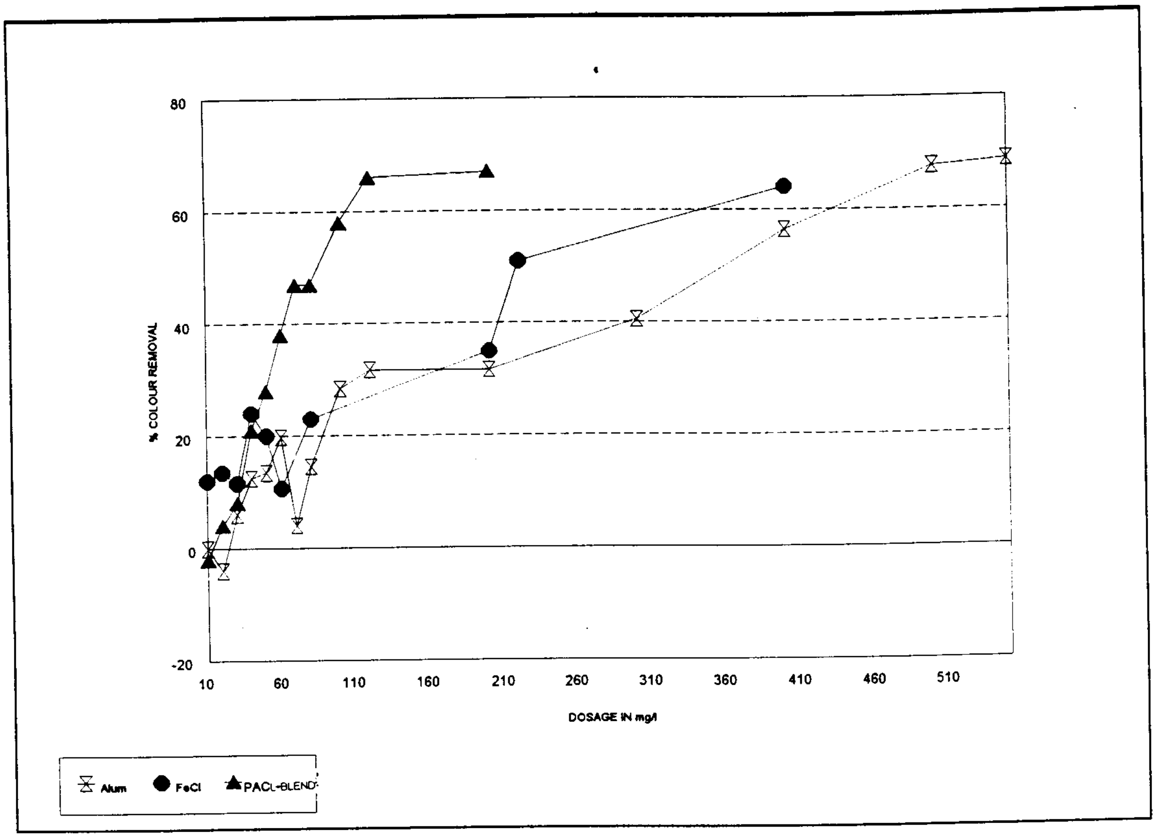

Figure 2: Comparison of colour removal with increasing dosages of three coagulants

Dosages of 120 mg/l PACl-blend gave far superior colour removal (+/-68%) than similar dosages of alum and ferric chloride (+/-30%). To obtain 68% colour removal with alum and ferric chloride dosages of 400 mg/l are needed. At these dosages pH was reduced to < 6. In Photo 1 the colour removal from secondary effluent by 60 mg/l PACl-blend and 500 mg/l alum is compared.

Big increases in colour removal were obtained with small increases in PACl-blend addition, while increase in colour removal was more gradual with alum and ferric chloride. That these two coagulants gave similar removal of colour was confirmed by plotting the percentage removals by alum and ferric chloride at selected dosages against each other (Figure 5, Appendix 2.). A straight line with gradient of 1 was obtained with $r^2 = 0.97$.

PHOTO 1: From Left: Secondary effluent; Secondary effluent + 60 mg/l PACl-blend Secondary effluent +500 mg/l alum

Corrosion requirements limit the dosages of alum and ferric chloride to 100 mg/l and 120 mg/l respectively and health requirements limit the PACl-blend dose to 60 mg/l. The mean and standard deviation (σ) for percentage removals obtained at these dosages at pH 7.6 was calculated and is reported in Table 5.

Table 5: Mean and standard deviation of colour removal with 3 coagulants

Alum at 100 mg/l	Mean- 26.2% σ - 3.8 %
Ferric chloride at 120 mg/l	Mean - 25.5 % σ- 13.2 %
PACl-blend at 60 mg/l:	Mean - 37.6% σ - 2.7 %

Dosing PACl-blend at 60 mg/l gave better colour removal than dosing alum at 100 mg/l and ferric chloride at 120 mg/l. The difference between colour removal obtained with alum and ferric chloride was marginal.

Comparison of removal of turbidity is reported in Table 6.

Table 6: Mean and standard deviation of turbidity removal with 3 coagulants

Alum at 100 mg/l	Mean- 35.57% σ - 36.3 %
Ferric chloride at 120 mg/l	Mean - 32.2 % σ- 14 %
PACl-blend at 60 mg/l:	Mean - 39.41% σ - 13.14 %

The difference in removal of turbidity is not as big as with colour removal, but 60 mg/l PACl-blend removes turbidity slightly better than 100 mg/l Alum or 120 mg/l ferric chloride.

Varying pH

The influence of pH on the efficiency of colour removal is compared for the three coagulants at constant dosages in Figure 3.

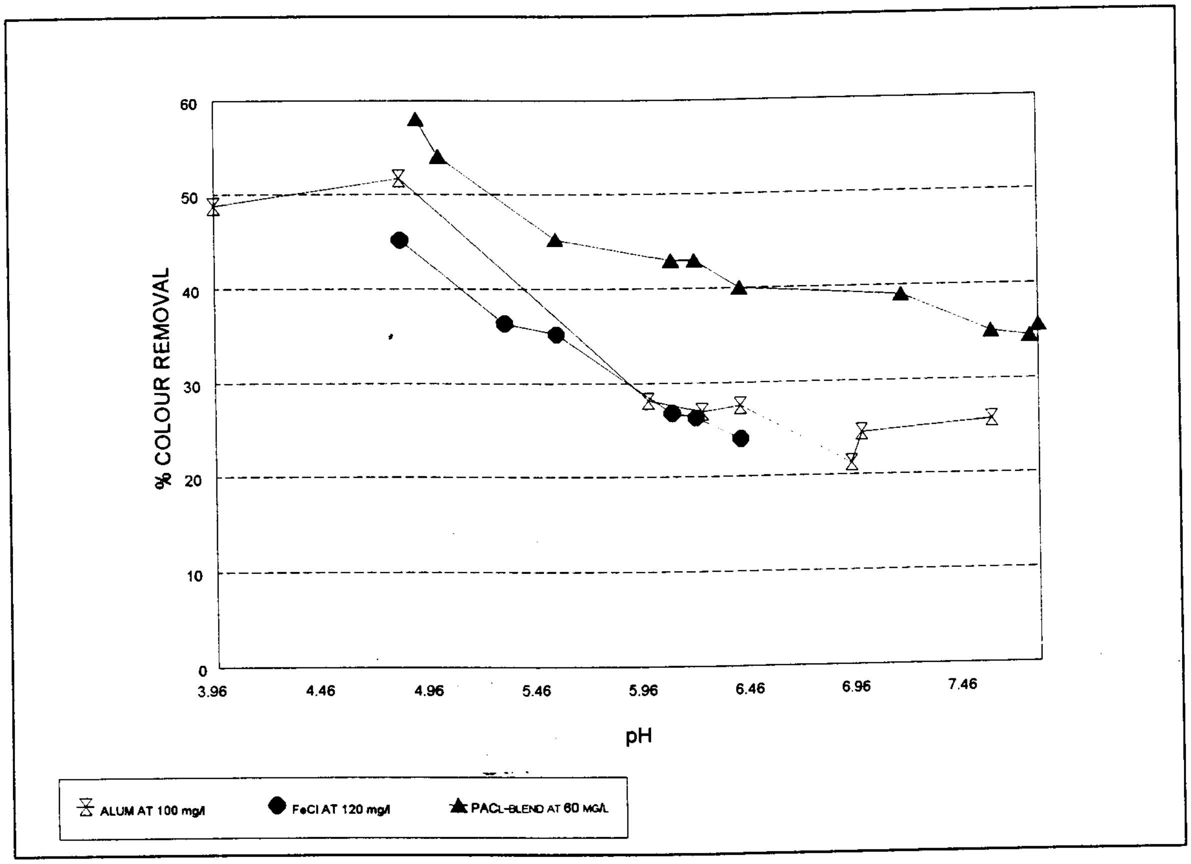

Figure 3: Comparison of the influence of pH on colour removal between three coagulants

Better removal was obtained with 60 mg/l PACl-blend than with 100 mg/l alum or 120 mg/l ferric chloride at all pH values. Similar removal efficiencies were again obtained with alum and ferric chloride. Colour removal was at least 20% higher at pH of around 5 than at pH 7.6 for all three coagulants.

Chemical quality

Table 7 shows a typical chemical analysis of secondary effluent from the abattoir.

Table 7: Chemical quality of secondary effluent

pH	7.65
Temperature	25°C
H_2CO_3 alkalinity	260 mg/l as $CaCO_3$
H_2CO_3 acidity	282 mg/l as $CaCO_3$
Total Calcium	70 mg/l as $CaCO_3$
Total Magnesium	70 mg/l as $CaCO_3$
Total Chloride	100 mg/l as Cl
Total Sulphate	35 mg/l as SO_4
TDS	664 mg/l
Conductivity	100 mS/m
Precipitation potential	-0.91 mg/l

The acidity and precipitation potential were calculated by the Stasoft Computer programme (Loewenthal *et al.*, 1988). The negative precipitation potential indicates the water is slightly aggressive and corrosive. The stabilisation dosage for a calcium carbonate precipitation potential of 4 mg/l was calculated for lime and was found to be 2.2 mg/l as $Ca(OH)_2$. Table 8 shows the resultant theoretical water characteristics after stabilisation.

Table 8: Secondary effluent quality after stabilisation

pH	7.78
Temperature	25°C
H_2CO_3 alkalinity	263 mg/l as $CaCO_3$
H_2CO_3 acidity	279 mg/l as $CaCO_3$
Total Calcium	73 mg/l as $CaCO_3$
Total Magnesium	70 mg/l as $CaCO_3$
Total Chloride	100 mg/l as Cl
Total Sulphate	35 mg/l as SO_4
TDS	664 mg/l
Conductivity	100 mS/m
Ionic Strength	0.016
Precipitation potential	4 mg/ l

The pH for optimum coagulation was 5. pH correction with sulphuric acid to reach this value increased the water sulphate content to 250 mg/l and decreased alkalinity to 20 mg/l. At dosages of 400 mg/l ferric chloride or alum the pH is reduced to <6, alkalinity to around 70 mg/l and chloride increased to around 260 mg/l (sulphate to about 150 mg/l). Coagulation with poly-electrolytes like poly-aluminium chloride and poly-amine had a comparatively small effect on chloride concentrations (Table 11).

Stabilisation with NaOH or $Ca(OH)_2$ would be needed to correct pH after coagulation with high metal dosages or pH correction. The lime dosage necessary to stabilise the water after each treatment to a calcium carbonate precipitation potential of 4 mg/l was determined by using the Stasoft programme. The Larson index ($\frac{(Cl + SO_4)}{Alkalinity}$) (Loewenthal *et al.*, 1986) was determined for each coagulant dosage and pH using alkalinity theoretically achieved after stabilisation. Lime stabilisation dosages and Larson index is reported in Table 9.

Table 9: Lime dosages calculated for stabilisation after each coagulation method, as well as Larson index values compared to removal efficiencies obtained.

Alum mg/l	$FeCl_3$ mg/l	PACl-blend mg/l	Larson index	% Colour removal	Lime mg/l	pH
400			1.1	81	130	5.4
100			0.75	31	300	4.7
	400		1.38	78	147	5
	120		0.75	59	284	5.7
		100	0.56	44.4	2	7.3
		60	0.5	41.9	2	7.3
		60	0.75	41	300	4.8

The Larson index increased from 0.49 to 0.5 with the dosage of 60 mg/l PACl-blend. The Larson index, after restabilisation with lime, of a water treated with 400 mg/l ferric chloride is 1.4 and 400 mg/l alum is 1.1. Dosages of alum and ferric chloride to these levels are not recommended.

The choice of coagulant

Coagulation with 60 mg/l PACl-blend is recommended as an initial tertiary treatment step. At 60 mg/l PACl-blend the water still contains 62.4% of the original colour and organic matter and needs to be treated with further processes before it will comply with the *insignificant health risk* standard.

Ozonation

An average of 5.86 mg ozone per minute was generated with the ozone generator at 0.5 A and 0.7 bar oxygen pressure. This value was used to determine applied ozone dosage for ozone demand and colour removal.

Ozone Demand

The ozone demand of secondary effluent and secondary effluent coagulated with 60 mg/l PACl-blend can be seen in Figure 4.

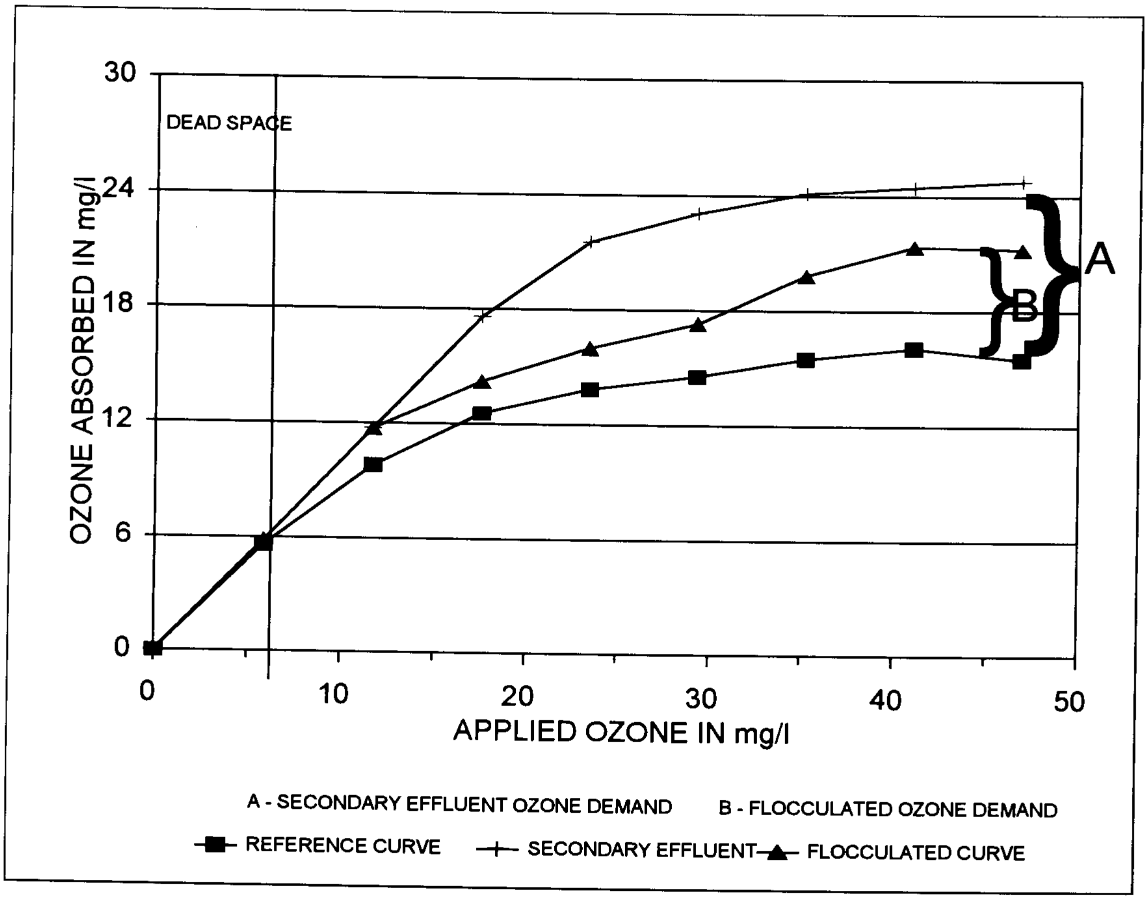

Figure 4: Reference and ozone demand curves for secondary effluent and effluent flocculated with 60 mg/l PACl-blend

The influence of the amount of dead space in the ozone transfer system on the apparent ozone absorbed by the water is represented by the first straight line portion where all three curves coincide. The difference between the reference and sample curves when the ozone absorbed becomes maximum in each case would give the ozone demand of the sample (Toerien, 1988). The ozone demand was about 8 mg/l for secondary effluent and 5.5 mg/l for flocculated water as shown in Figure 4. The difference in ozone demand between secondary effluent and coagulated effluent means that coagulation would reduce ozone dose. Another advantage is that it may absorb variations in raw water quality, avoiding continual adjustment of ozone dose.

Ozone absorbed and colour removal: Relationship

The reduction of colour from secondary effluent with ozone was non-linear, as reported by Juby and Botha (1994), with significant reductions at low ozone dosages. The removal values were fitted to a power curve with the following formula: $y = 23.6\,x^{0.43}$ $r^2 = 0.989$. The observed values are plotted with the theoretical curve in Figure 5.

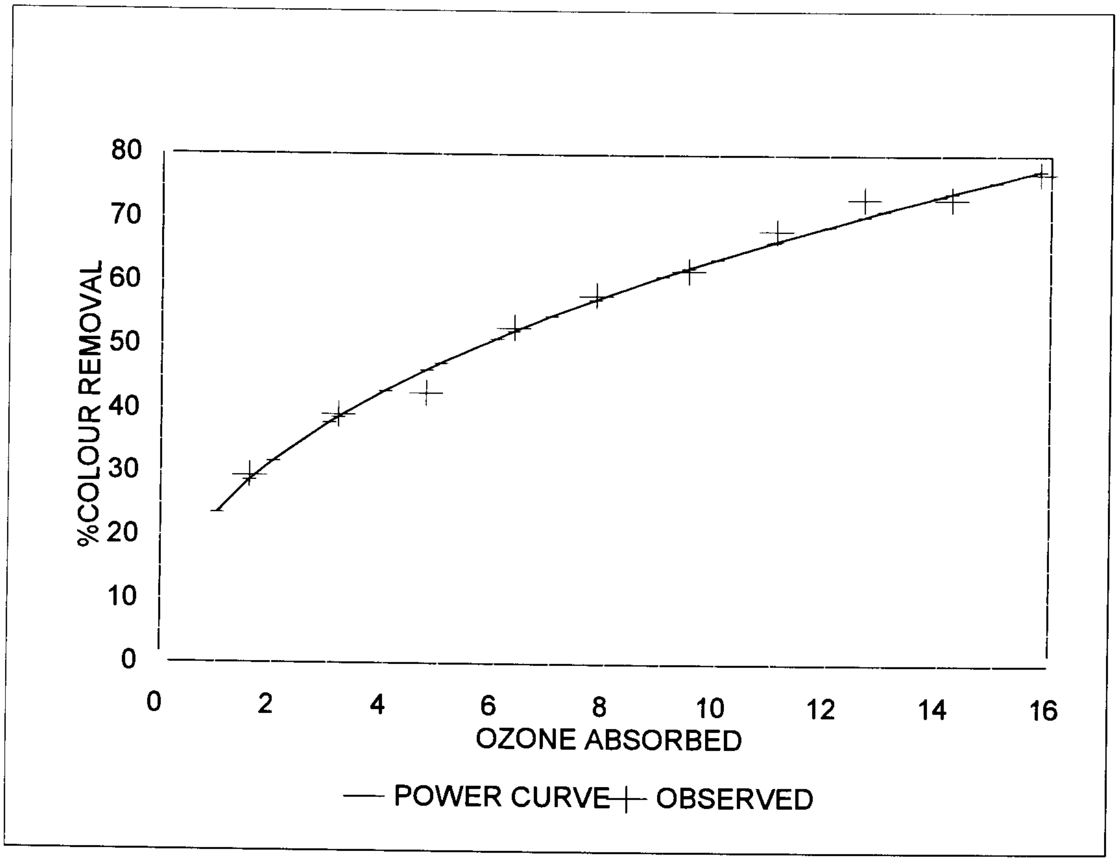

Figure 5: Comparison of theoretical and actual reduction in colour with increase in ozone absorbed for secondary effluent

Fitting the colour removal efficiency to a theoretical formula would enable predictions to be made on the ozone dose necessary should the colour in the secondary effluent vary. The colour reduction rate decreased with higher dosages. According to Tan and Amy (1991) a refractory fraction of colour will remain.

The colour removal obtained at the secondary effluent ozone demand dose of 8 mg/l is shown in Photo 2 along with secondary effluent colour and colour after ozonation followed with coagulation.

PHOTO 2: From left: Secondary effluent; Secondary effluent + 8 mg/l ozone; Secondary effluent + 8mg/l ozone + 60 mg/l PACl-blend

Activated carbon adsorption

In Figure 6 the colour reduction in coagulated and ozonated secondary effluent by adsorption on increasing dosages of activated carbon is shown.

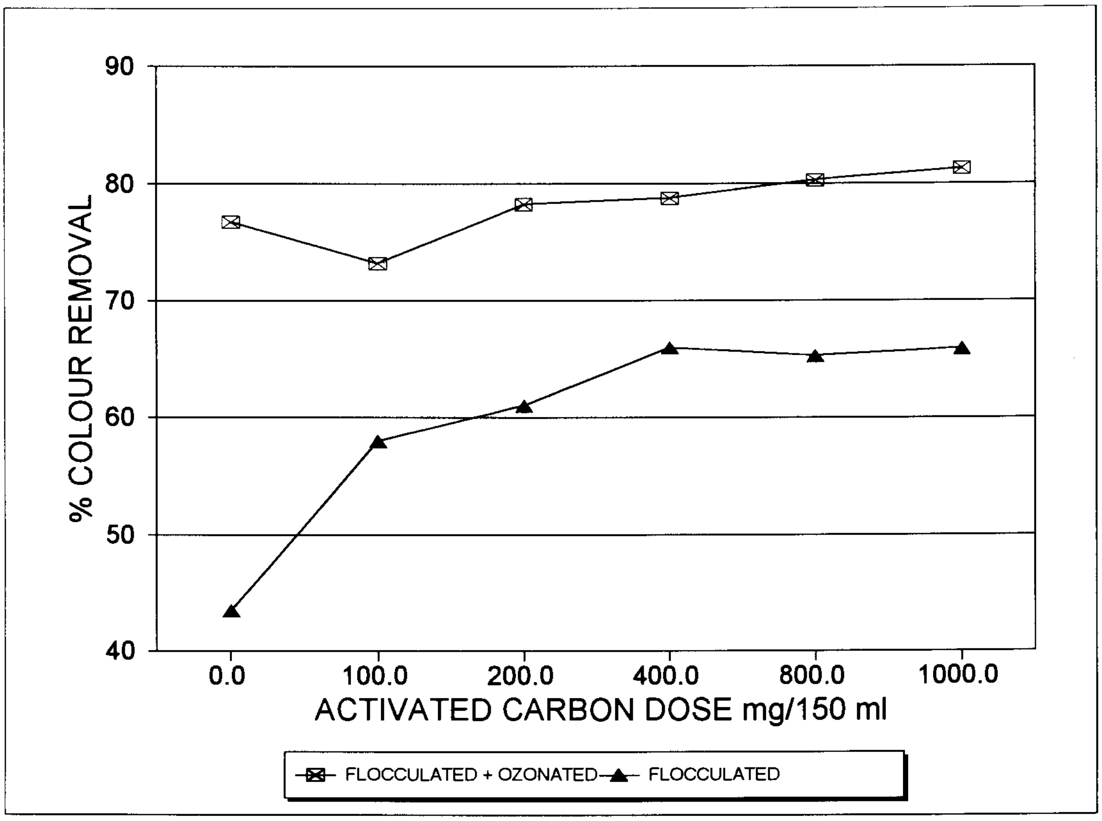

Figure 6: Comparison of colour removal with carbon adsorption of flocculated and flocculated plus ozonated secondary effluent

The colour removal in the flocculated sample was increased from 40% to 64% by the maximum activated carbon added. The increase in removal was 20% at 400 mg/150 ml, but the slope of this curve decreased at higher dosages. The carbon probably reached its adsorption capacity for the coloured matter around this dosage. Colour removal from the ozonated water was increased from 77% to 81% by the maximum activated carbon added. The gradient of this curve shows adsorption capacity for colour from this water is very low.

Breakpoint chlorination

The chlorine dosages needed to reach breakpoint in secondary effluent, coagulated and ozonated effluents are reported in Table 10 (See Figures 8-10 in Appendix 2). These values were obtained by measuring the chlorine residuals with the DPD ferrous titrimetric method at pH 7.6 and 20°C.

Table 10: Breakpoint chlorine dosages to obtain free residual chlorine

Sample	**Breakpoint chlorine dosage**
Secondary effluent	120 mg/l
Secondary effluent + 60 mg/l PACl-blend	90 mg/l
Secondary effluent + 60 mg/l PACl-blend +5.5 mg/l	75 mg/l

The breakpoint chlorination could be reduced from 120 mg/l to 90 mg/l by removal of DOM through coagulation with 60 mg/l PACl-blend. Ozonation and filtration reduced the breakpoint further to about 75 mg/l. This is still quite high and could be an indication of ammonia remaining in the water after treatment with coagulation and ozone

Comparative Removal

Coagulation with 60 mg/l, PACl-blend, ozonation at 5.5 mg/l followed by filtration and contacting activated carbon at 1000 mg/150 ml for 12 hours was performed on a sample of secondary effluent. The influence of each treatment step on the parameters influencing the health, aesthetic and economic acceptability of the water was determined. These parameters were compared to the guideline values in Table 11.

Table 11: The water quality produced by the selected treatment processes, compared to guidelines for *insignificant health risk* and corrosion

	Guideline values	Secondary effluent	PACl-blend at 60mg/l	Ozonation 5.5 mg/l+ filter	Activated Carb. 1000mg/150ml
TDS-mg/l	2000	664	664	664	664
Alkalinity-mg/l $CaCO_3$		300	300	300	300
Chloride-mg/l	600	110	112	112	112
Larson- index	0.2	0.49	0.5	0.5	0.5
Hardness- mg/l $CaCO_3$	200	120	120	120	120
pH	5.5-9.3	7.65	7.65	7.8	7.5
Turbidity-NTU	5	5.2	3.6	1.9	1.9
Colour- Hazen	20	176	110	41	33
DOC-mg/l	20	91	76	50	38
Plate count cfu/100 ml	1000	2000000	1000000	50000	Not Done

The TDS, alkalinity, hardness and sulphate concentrations were not affected significantly by any of the treatment processes. A slight increase in chloride ion concentration was due to the addition of PACl-blend that released a small amount of counter ions. This increased the Larson index by 0.01.

The dosage of 60 mg/l PACl-blend reduced turbidity from 5.2 NTU to 3.6 NTU (by 30%). Small pin flocs appeared in the coagulated sample after ozonation. This increase in turbidity was not measured before filtration. After filtration, the turbidity was improved from 3.6 NTU to 1.9 NTU. This shows that ozonation has a positive effect on turbidity removal if a filtration can be included after ozonation. Batch contacting the granular activated carbon in beakers did not increase turbidity.

DOC was reduced from 91 mg/l to 76 mg/l by coagulation (16%). Ozonation and filtration reduced the DOC by a further 29% to 50 mg/l. DOC removal with activated carbon adsorption for 1000 mg/150 ml was 13%. The DOC was reduced by a total of 58% by all three steps. The total DOC removal with this dosage of activated carbon was 61% when coagulated but unozonated water was used. The unozonated DOM therefore appears to adsorb better on the activated carbon. This is possibly due to the oxidation of organic matter to smaller more polar entities that does not adsorb well on activated carbon (Weber, 1984).

The biodegradability of the organic matter and the development of BAC was not examined in this study. The dosage ratio in this experiment of about 0.8 mg O_3/mg DOC may have to be increased to the recommended 1-2 mg ozone/mg TOC. This value was reported (Juby and Botha, 1994; Goel *et al.*, 1995) to be necessary to increase biodegradability of humic matter.

Coagulation reduced colour, approximately by the percentage predicted in Table 5, to 110 Hazen. Ozonation reduced this colour to 41 Hazen. Adsorption on activated carbon reduced this value to 33 Hazen which is still higher than the recommended 20. This colour could possibly be reduced further if BAC develops. Photo 3 shows the reduction in colour from secondary effluent with flocculation and ozonation.

PHOTO 3: From Left: Secondary effluent; Secondary effluent + 60 mg/l PACl-blend; Secondary effluent + 60 mg/l PACl-blend + 5.5 mg/l Ozone

Bacteria reduction was 50% after coagulation and 95.26% after ozonation. Ozonation was not employed as a disinfecting step however. Bacteria levels could increase in the final water if BAC develops. A terminal disinfectant step is necessary.

5. DISCUSSION

Comparison of coagulants.

Better removals of colour and turbidity were obtained at 60 mg/l PACl-blend than with alum or ferric chloride at 100 and 120 mg/l respectively. Optimum dosages for colour removal were also found to be optimum for turbidity removal in this experiment as was predicted by Semmens and Field (1980) and Dempsey *et al.*, (1985).

The superior performance by PACl-blend (tables 5 and 6) can be explained by the fact that stoichiometric metal coagulant and polymer coagulant dosages are normally required with precipitation of DOM (Vik *et al.*, 1985). The amount of coagulant added would be proportional to the amount of reaction sites on the organic matter (Amirtharajah *et al.*, 1993). The charge density provided by the poly-aluminium chloride and poly-amine blend, PACl-blend, is high (Dempsey *et al.*, 1985), therefore less is needed to reach the optimum charge addition than with ferric chloride or alum. Secondly, different fractions of the humic matter could be more amenable to removal by different coagulants (Randtke and McCarty, 1979). A blend like PACl-blend could incorporate the coagulation effect of both poly-amine and poly-aluminium chloride and could therefore be more effective for colour removal.

The pH was reduced when ferric chloride and alum were used due to depletion of hydroxide to form hydrolysis intermediates and hydroxide precipitate (Hong-Xiao and Stumm, 1987). This reduction in pH could play a role in the increase in colour removal obtained at higher dosages of metal salts. The length and charge distribution of the hydrolysis intermediates-metal species formed with metal coagulants (Stephenson and Duff, 1996) would be determined by pH and would not necessarily always be consistent or optimum. This would explain high variability in results obtained with colour removal with ferric chloride.

Optimum removal under pH conditions of around 5 was found by several authors like Edzwald *et al.* (1977), Narkis and Rebhun (1983) and Christman and Ghassemi (1966). This can be explained by the destabilising effect of reducing pH on organic matter (Kuo and Amy, 1988). Reducing the pH of solutions before addition of all coagulants improved removal of colour (Figure 3). The humic matter would be partially or completely dissolved due to negatively charged groups (Vik *et al.*, 1985). The stoichiometry of the precipitation reaction could be altered by decreasing the negative sites on the molecules by protonation when the pH was reduced to 5 (Amirtharajah *et al.*, 1993). Less coagulant was needed to destabilise the same amount of DOM.

The colour causing humic matter in the secondary effluent from Johannesburg abattoir appeared to react in a charge neutralisation and precipitation reaction with the coagulants. Polymeric hydroxyl intermediates, formed when metal salts are added to water, as well as synthetic polymers could precipitate the humic matter (Dempsey et. al., 1985). Higher molecular weight, less oxygenated compounds such as humic matter is primarily removed by precipitation, while smaller highly charged DOM by sorption onto a hydroxide precipitate (Edwards *et al.*, 1994). That pre-formed polymers could remove colour better than the metal species indicated that the sorption reaction did not play a big role and most of the DOM would be longer chain humic matter.

Chemical quality

The buffer capacity of the secondary effluent is high (alkalinity-Table 4) and this increased the stability of the humic matter (Moyers and Wu, 1985). Very high acid dosages were needed to overcome this alkalinity to reduce pH to 5. This increased the chlorine or sulphate ion concentrations to unacceptable levels for corrosion control (Table 9).

Poly-aluminium chloride and poly-amine molecules both have only one counter ion (Cl-) per polymer, while metal salts have to release up to three chloride ions per monomer to form poly-hydroxyl entities. The impact on the corrosivity of the water is far greater to obtain the similar colour removal shown in Figure 2. The pH would be lowered with high dosages of metal coagulants, requiring restabilisation of the water at a later stage, which would need another filtration and sludge disposal stage (Constantine, 1982).

Ozonation

Colour and DOM matter can be removed by adjusting the pH to 5 or by very high dosages of ferric chloride, alum or PACl-blend. Adjusting the pH and coagulating with the first two options would lead to water that is unacceptable for economic reasons. The last coagulant would be dosed in excess of health recommendations. Additional treatment methods are necessary to reduce colour and DOM to within guideline levels.

Ozonation was investigated for its effectiveness in reducing colour. Satisfactory reduction in colour (Figure 5) can be achieved with ozonation alone. This colour removal would be due to the destruction of double bonds and chromophores (Razumovski and Zaikov, 1984). Ozonation to this level will also possibly enhance turbidity removal with coagulation (Figure 7, Appendix 2). However, DOM would not necessarily be reduced as well (Constantine, 1982).

The products of ozonation would of lower molecular weight and more charged than humic matter (McCarthy and Smith, 1974). The efficiency of coagulating this DOM would be reduced. Therefore, the bulk of the DOM should be removed with coagulation before ozonation. This was done by coagulation with 60 mg/l PACl-blend. Furthermore, ozonation is costly and reducing the ozone demand by removing DOM will reduce this cost. Removing turbidity before ozonation would also facilitate any disinfection by ozone by reducing any shielding effect by suspended particles (Train, 1979).

The pin floc formation seen after ozonation of flocculated water (Table 11) could be explained by ozone neutralising negative colloids, thereby destabilising them and enhancing coagulation (McCarthy and Smith, 1974). Ozonation can also destabilise organic matter adsorbed on colloids, thereby also decreasing their stability (Grasso and Weber, 1988; Edwards *et al.*, 1994). When the secondary effluent was coagulated and then ozonated, the resultant turbidity could easily be removed by filtration only and turbidity was improved from 3.6 NTU in the flocculated water to 1.9 NTU.

The DOC was simultaneously reduced from 75mg/l to 50 mg/l with ozonation and filtration (Table 11).This removal of DOM could be due to the destabilisation of organic colloidal matter, pin floc formation and subsequent removal with filtration. It could also be due to polymerisation of organic matter due to ozonation that could create some hydrophobic molecules that could coagulate (Chang and Singer, 1991). Constantine (1982) and Edwards *et al.* (1994) reported that significant fractions of organic matter would be oxidised to CO2 only when very high ozone dosages and long reaction periods are applied. The ozone concentrations used in this study is not high enough to reduce DOM in this manner

The DOM would be in a more biodegradable form than before ozonation (Juby and Botha, 1994). This could cause bacterial regrowth (Symons, 1980). The oxidised organic matter is also very reactive towards forming chlorinated hydrocarbons (Moyers and Wu, 1985). These compounds are normally volatile and can cause odours

Activated carbon adsorption**.**

It was shown that a different fraction of DOM may be more amenable to adsorption removal than removal with coagulation. Pre-precipitation altered the relative percentages of most adsorbable and less adsorbable (Weber and Jodellah, 1985). Ozonation seemed to have had a negative effect on adsorption of DOC (Table 11). Ozonation should have oxidised particles to low molecular weight, polar entities that are generally not adsorbed well (Symons, 1980).

Because of the increase in biodegradability, ozonation should enhance the development of BAC (Weber, 1984). This process should be utilised, rather than suppressed, since it has proved to give much higher organic matter removal from coloured water than adsorption without biological activation (Constantine, 1982). BAC could theoretically increase DOC removal from coagulated and ozonated secondary effluent from 13% to a possible 60% (Juby and Botha, 1994). This would reduce the DOC to <20 mg/l which is within the guideline value in Table 11.

Breakpoint chlorination

Coagulation and ozonation reduced the breakpoint chlorination from 120 to 70 mg/l. This would be the amount necessary to obtain a free residual chlorine for disinfection after these two steps. Adsorption on activated carbon and BAC would reduce this breakpoint further by reducing DOM that constitutes chlorine demand (Krasner *et al.*, 1989).

The high breakpoint of 75 mg/l is probably due to the presence of ammonia (Hart, 1978). Ozone does not reduce ammonia unless the pH is above 9 (Grachok *et al.*, 1990). This ammonia would be stripped by chlorinating to breakpoint, where the stable monochloramine should form. Consideration could be given to employing chloramination as a disinfection step (National Institute for Water Research, 1981). Longer contact times would be necessary, but disinfectant residuals would be more stable.

6. CONCLUSION

Comparison between alum, ferric chloride and PACl-blend as coagulants for colour removal showed that PACl-blend resulted in a better colour removal at half the dosages of the other two coagulants (Table 5). Furthermore, PACl-blend does not impact on the pH of the water and release significantly less (Table 6) amounts of counter ions than alum and ferric chloride (Table 1).

1. Coagulation with PACl-blend at 60 mg/l and settlement should be an initial treatment step. Either ferric chloride or alum could be used as a second choice since their performance was similar.

Reducing the coagulating pH from 7.6 to 5 increased colour removal with coagulation by 20% at constant coagulant dosages. The high acid dosages needed to overcome the buffer capacity of the water to achieve this increased the chloride and sulphate ion concentration to 3 or 4 times the recommended values for corrosion control.

2. Due to the high buffer capacity, adjusting the pH to optimise coagulation is not advisable.

Ozonation and filtration improved colour and organic matter removal to levels attained by very high dosages of coagulants or better. The relationship defined in this study could be used in practice to adjust ozone dosages for variations in colour of the secondary effluent. DOM was also reduced after filtration. The chemical quality of the water was not affected by ozonation.

3. Ozonation and filtration should be included in the treatment sequence to reduce colour and organic material and increase the biodegradability of the DOM

Activated carbon adsorption was slightly less effective in DOM removal after ozonation than after just flocculation. However, colour removal was better with the ozonation step included.

4. DOM levels could possibly be reduced to within the guideline values with ozone and activated carbon if BAC is allowed to develop.

The tertiary treatment recommended to renovate the secondary effluent from Johannesburg abattoir to comply with water quality of *insignificant health risk* should consist of:

- Coagulation with 60 mg/l PACl-blend and flocculation at ambient pH.
- Settlement.
- Ozonation at 5.5 mg/l (or higher to increase biodegradability).
- Filtration.
- Activated carbon adsorption with provision for biologically activated carbon to develop.
- Disinfection with either free residual chlorination or chloramination.

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APPENDIX 1

Table 1:Proposed water quality criteria of the Department of National Health and Population Development (Pieterse, 1989).

Determinant	Unit	Limit for *no health risk*	Limit for *insignificant health risk*	Limit for *low health risk*
Physical/Organoleptical				
Colour	mg/l Pt	20		
Conductivity	mS/m	70	300	400
DOC	mg/l C	5	10	20
Dissolved oxygen	% Sat	70	30	10
Odour	TON	1	5	10
pH	unit	6.0-9.0	5.5-9.5	<4 or>11
Taste	TTN	1	5	10
Temperature	°C	<25	<30	<40
Turbidity	NTU	1	5	10
Microbiological				
Standard Plate Count	counts/ ml	<100	1000	10000
Total Coliform	counts/ 100ml	0	3	100
Feacal Coliform	counts/ 100ml	0	1	10
Clostridium Perfringes	counts/ 100ml	0	1	10
Coliphages	counts/ 100mm	0	10	100
Enteric Viruses	TClO/1 0 1	0	1	10
Macro Variables				
Aluminium	mg/l	0.15	0.5	1.0
Ammonia	mg/l	1.0	2.0	4.0
Barium	mg/l	0.5	1.0	2.0
Boron	mg/l	0.5	2.0	4.0
Bromide	mg/l	1.0	3.0	6.0
Calcium	mg/l	150	200	400
Cerium	mg/l	1.0	2.0	4.0
Chloride	mg/l	250	600	1200
Copper	mg/l	0.5	1.0	2.0
Fluoride	mg/l	1.0	1.5	3.0

Hardness	mg/l	20-300	650	1300
Iodide	mg/l	0.5	1.0	2.0
Iron	mg/l	0.1	1.0	2.0
Lithium	mg/l	2.5	5.0	10.0
Magnesium	mg/l	70	100	200
Manganese	mg/l	0.05	1.0	2.0
Nitrates	mg/l	6.0	10.0	20.0
Potassium	mg/l	200	400	800
Sodium	mg/l	100	400	800
Sulphate	mg/l	200	600	1200
Uranium	mg/l	1	4	8
Zinc	mg/l	1	5	10

In Figure 1, the variation in turbidity of the secondary effluent is compared with turbidity requirements for water with no, insignificant and low health risks.

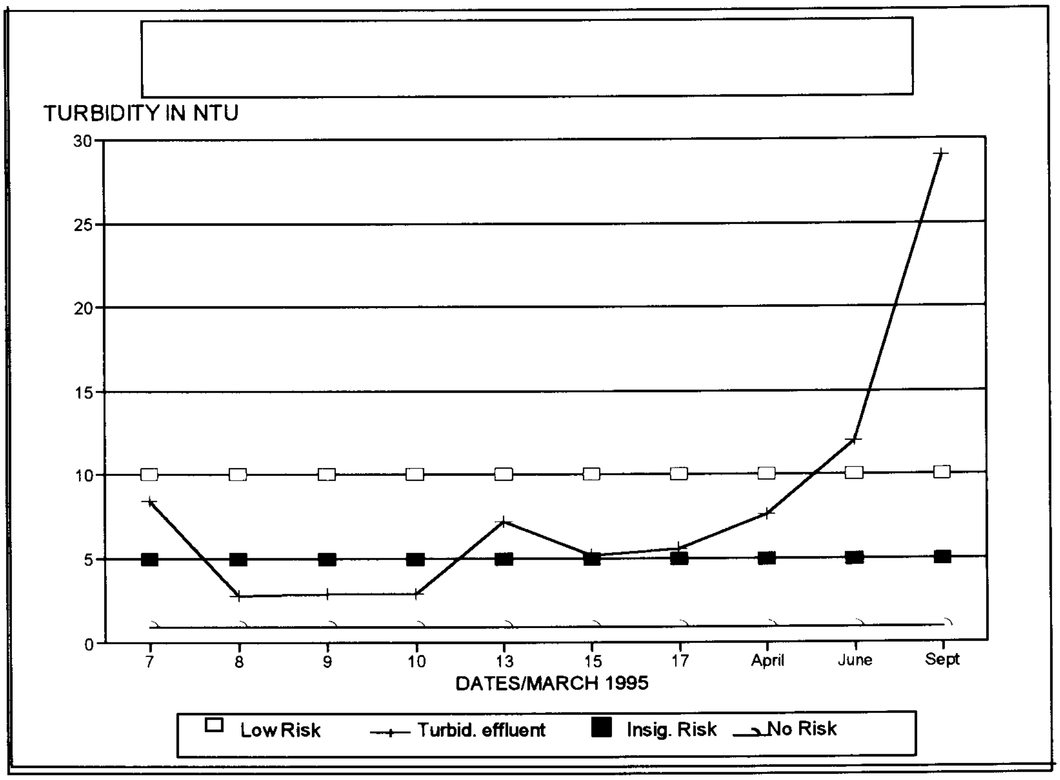
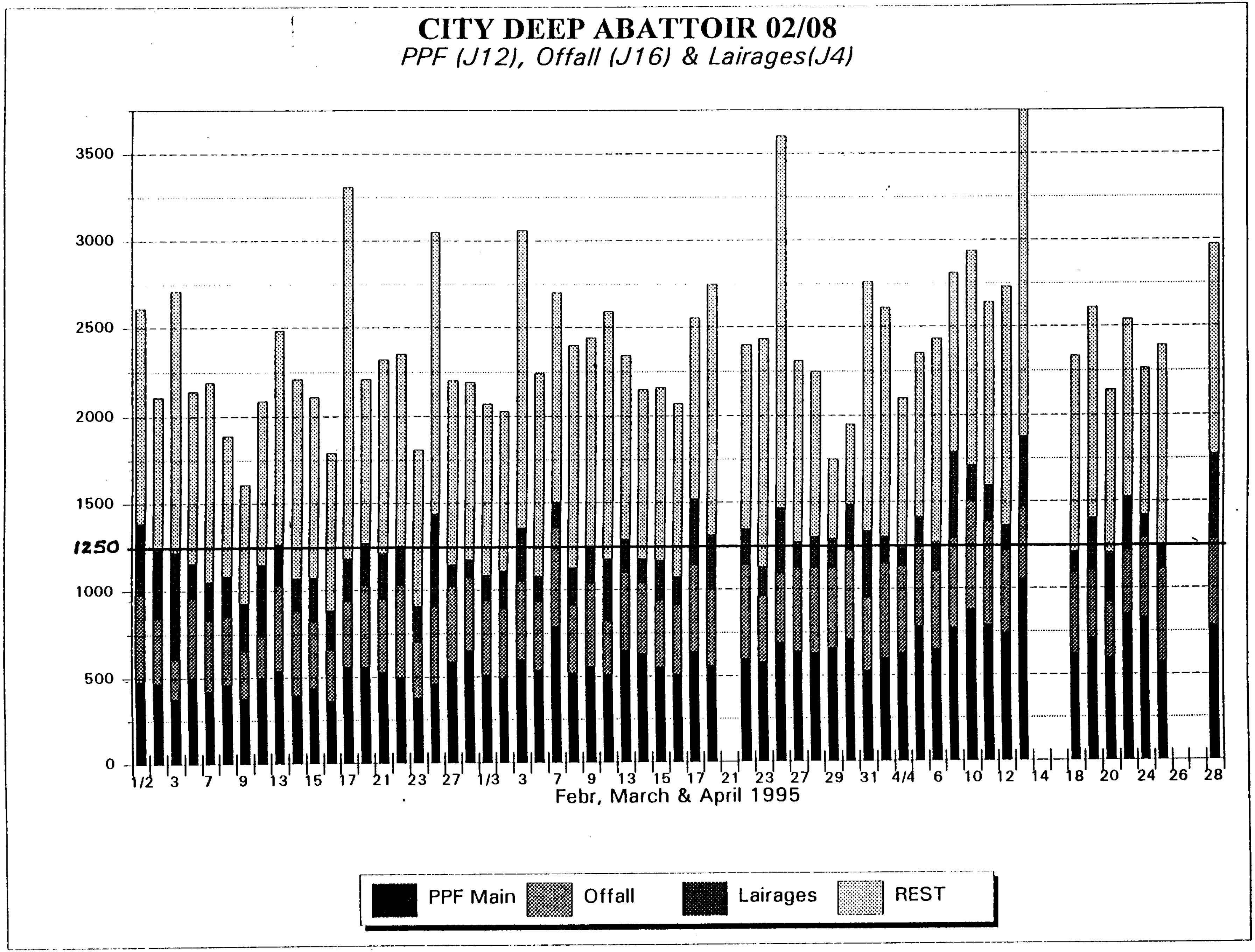


FIGURE 1: The variation in turbidity against guideline limits for water of *no-, insignificant* and *low health risks.*

The dates of 13 March and dates in April, June and September were on Mondays, when clarifier was anaerobic



CITY DEEP ABATTOIR 02/08

PPF (J12), Offall (J16) & Lairages(J4)

Figure 2: Water consumption of the Johannesburg abattoir (Van Heerden, 1994)

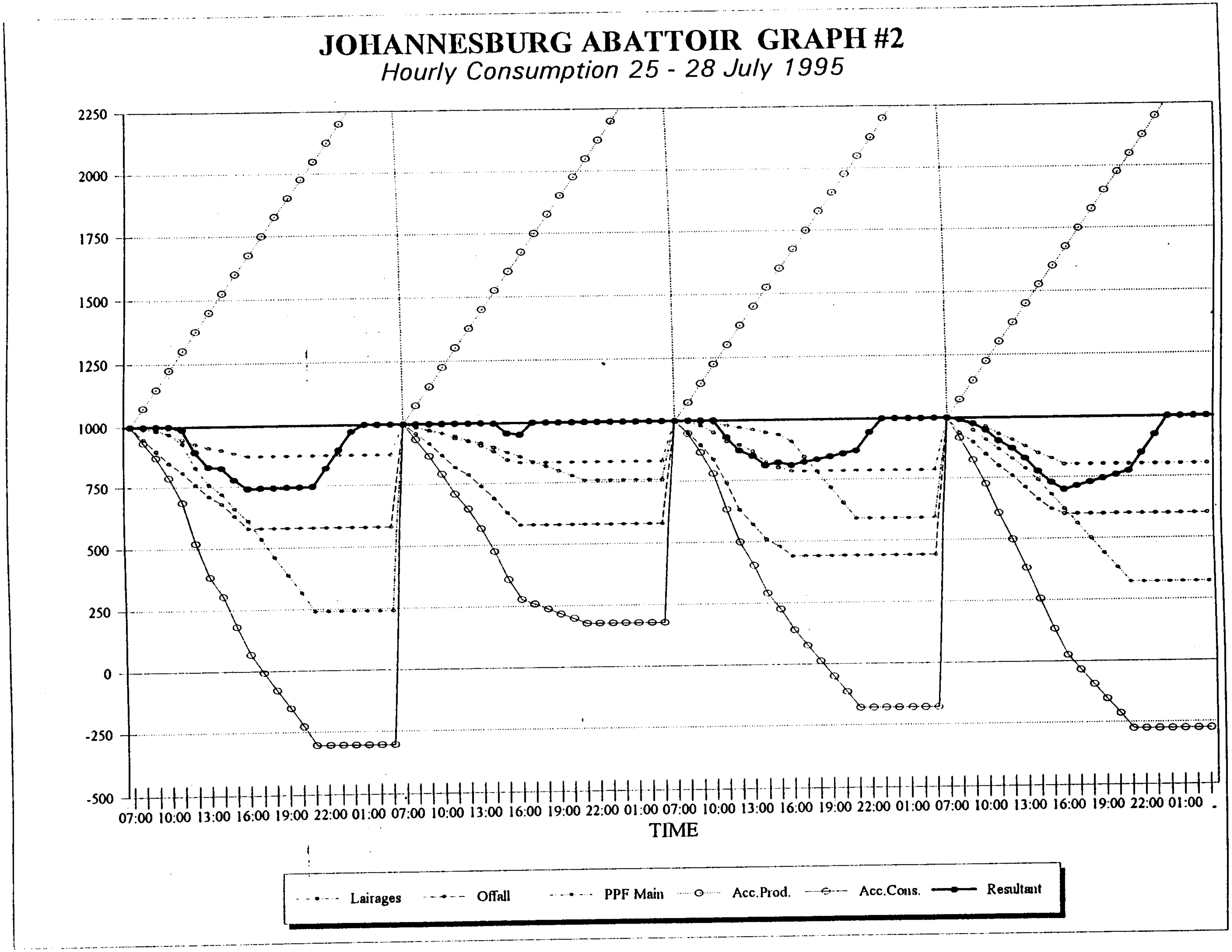


Figure 3: Effluent production by the different sections of the Johannesburg abattoir and resultant effluent available for re-use (Van Heerden, 1994).

APPENDIX 2

The nature of secondary effluent DOM

The predominantly humic nature of the DOM in the secondary effluent was proven by performing a UV absorption analysis (Department of Microbiology, University of Pretoria). An absorption profile (Figure 1) was obtained by Morrison (1996) on a coloured surface water from the Southern Cape. The waters from this area contains high colour and humic material concentrations. This profile was similar to the absorption profile drawn on secondary effluent (Figure 2).

Figure 1: UV absorption profile of Southern Cape water (Morrison, 1996)

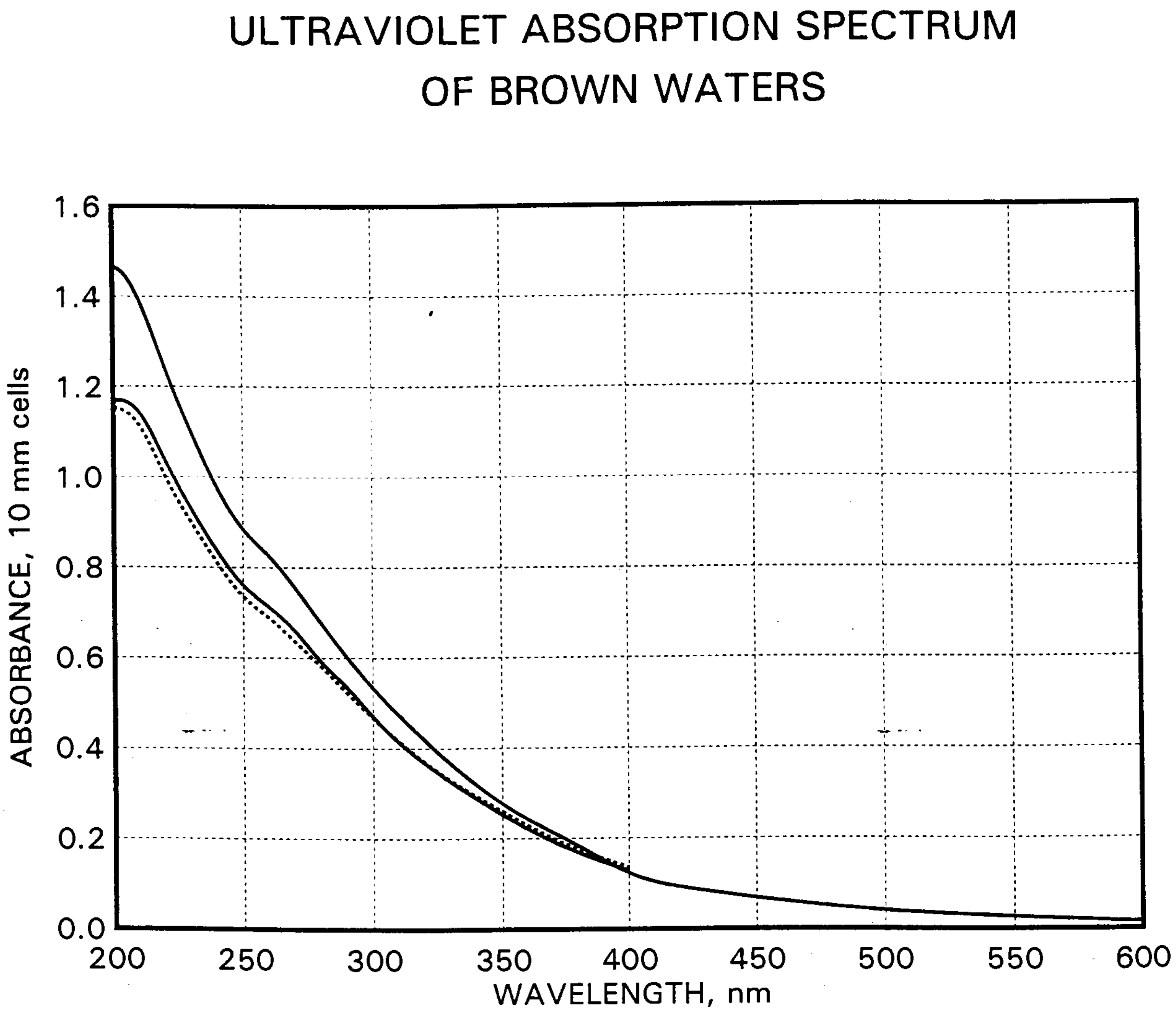
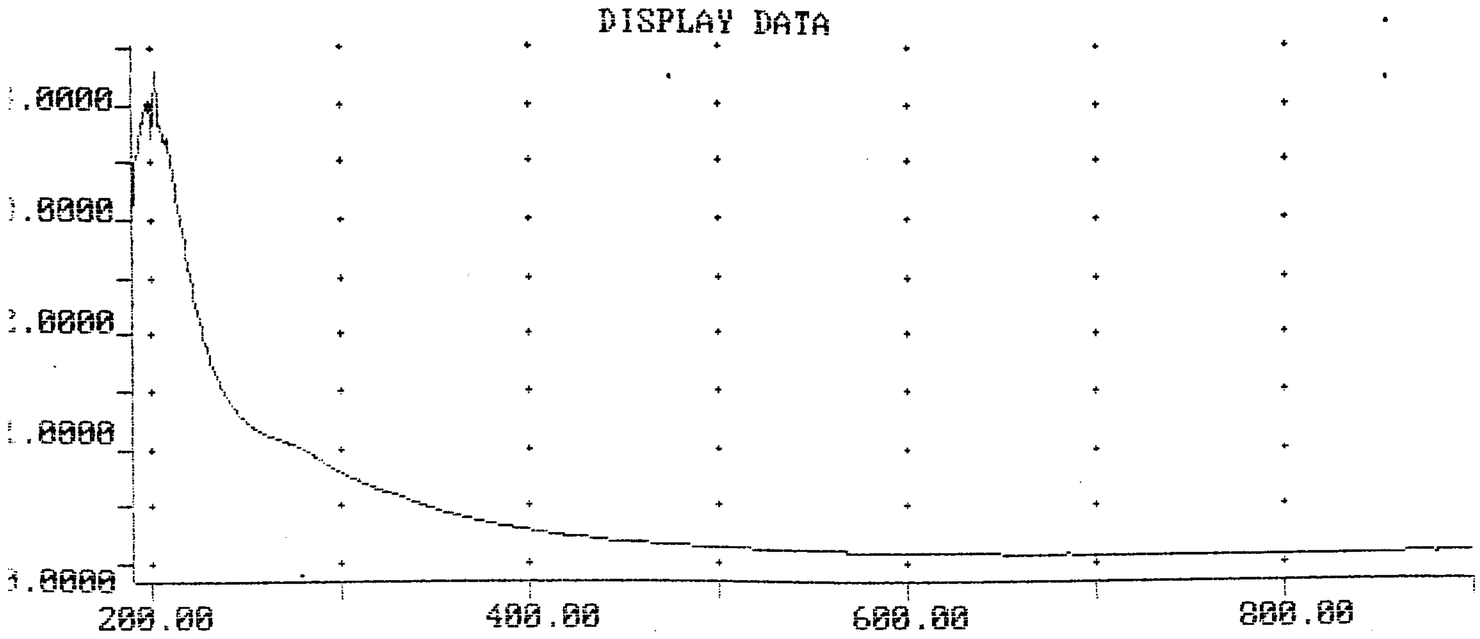


Figure 2: UV absorption profile of secondary effluent.



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S                : -0.1534  ->  4.5090          NM     :  190.00  ->  900.00

e name :   Current#
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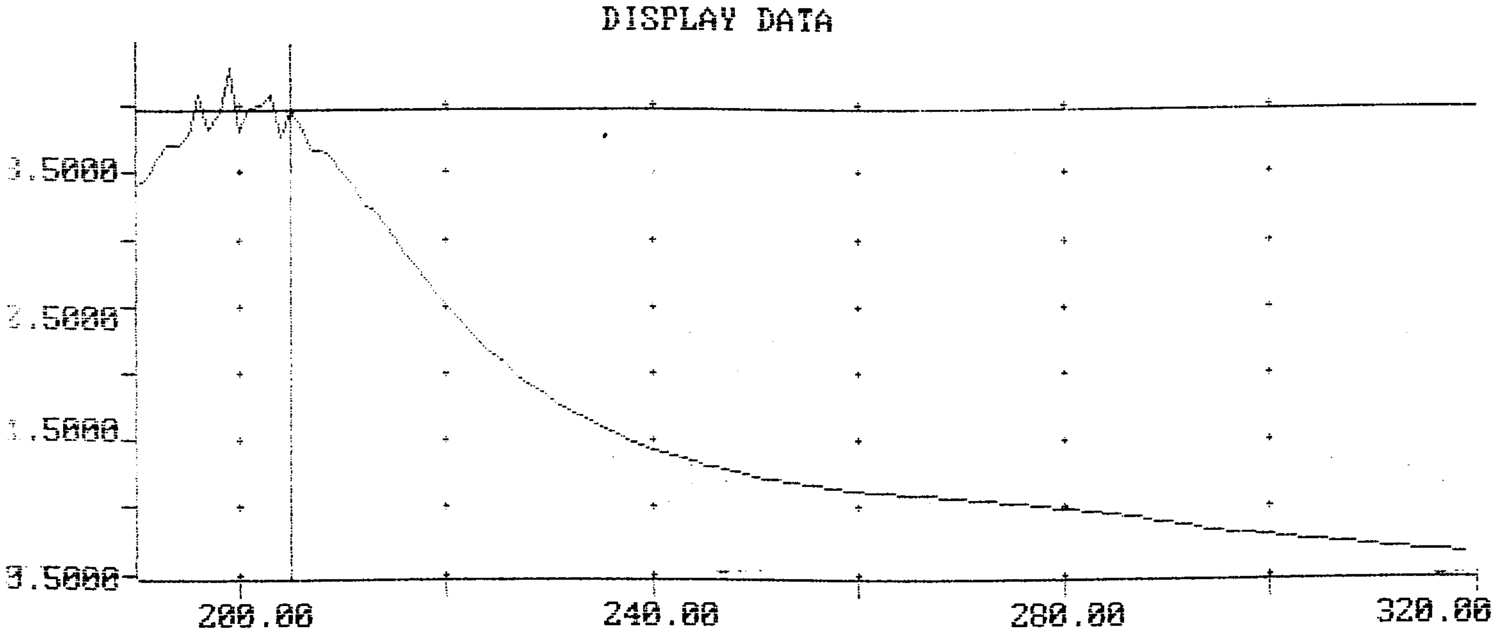


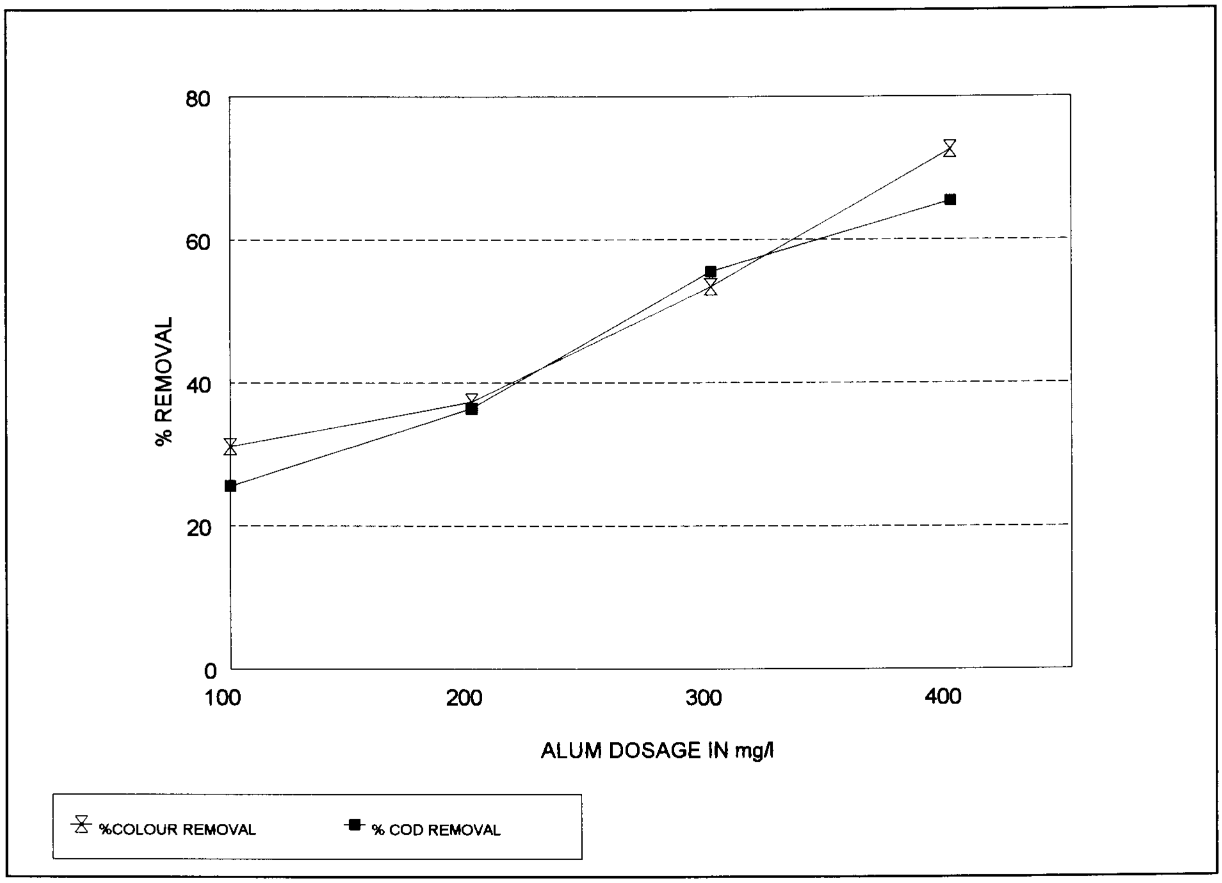
```
BS               :  0.4626  ->  4.4700          NM     :  190.00  ->  320.00

    X        Y        X        Y        X        Y        X        Y
-----------------------------------------------------------------------
  320.00   0.6448   319.00   0.6490   318.00   0.6559   317.00   0.6611
  316.00   0.6671   315.00   0.6733   314.00   0.6793   313.00   0.6860
  312.00   0.6916   311.00   0.6977   310.00   0.7047   309.00   0.7121
  308.00   0.7215   307.00   0.7267   306.00   0.7336   305.00   0.7417
  304.00   0.7498   303.00   0.7578   302.00   0.7651   301.00   0.7735
  300.00   0.7820   299.00   0.7910   298.00   0.8000   297.00   0.8093
  296.00   0.8185   295.00   0.8289   294.00   0.8392   293.00   0.8493
  292.00   0.8606   291.00   0.8716   290.00   0.8838   289.00   0.8949
  288.00   0.9067   287.00   0.9192   286.00   0.9301   285.00   0.9412
```

UV absorbance of a sample at 254 nm usually indicates the presence of conjugated and cumulative double bonds (Juby and Botha, 1994). A high percentage of the absorbance could be due to conjugation due to the presence of humic material.

<u>Use of colour as indicator for organic material</u>

The correlation between colour removal and organic material removal with coagulation is shown in Figure 3. Since similar colour removal could be achieved with dosages of 120 mg/l U3500 and 400-500 mg/l alum or ferric chloirde similar organic material removal should be obtained.



<u>Figure 3: The relationship between removal of colour and COD from secondary effluent with coagulation with alum.</u>

Humic material, being long chain organic molecules with only some charged groups, could be slightly hydophobic and therefore easily destabilised by complexation of the charged gorups and precipitated. Therefore the colour containing DOM are removed with coagulation and results in a reduction of both colour and organic matter.

The relationship between colour and COD removal with activated carbon adsorption is not as strong as in the case of coagulation (Figure 4).

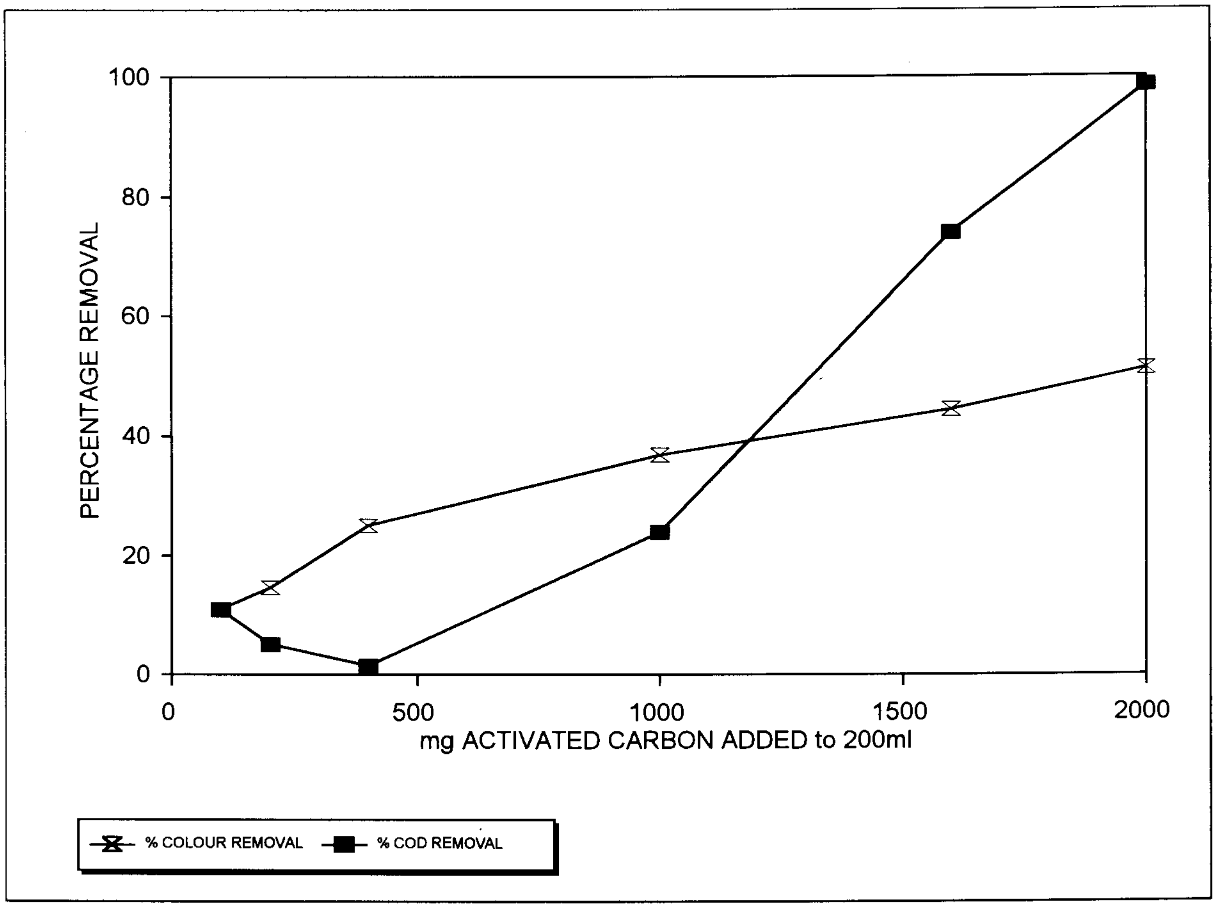


Figure 4: The relationship between colour and COD removal from secondary effluent with adsorption on activated carbon

This could be due to activated carbon adsorbing some organic molecules with no colour constituents to a greater extent than the humic molecules. The pore size distribution of the activated carbon could have influenced removal of the larger organic molecules (Sierka *et al,* 1989; El-Rehaili and Weber, 1987). PHO 12/40 is a coconut based activated carbon with a small pore size and low capacity for adsorption of humic matter. Colour removal would be improved using a peat-, wood- or bitumen-coal based activated carbon (Nel, 1996)

Since the colour causing conjugation in humic molecules would be destroyed by ozonation, colour would not be a good indicator of organc material removal after ozonation (Owen *et al.*, 1995). This was illustrated by the fact that 78% reduction in colour was observed with an ozone dose of 5.5 mg/l, but there was only a 45% reduction in COD (Table 7). This removal is probably due to destabilisation (Chang and Singer, 1991) of organic colloids and removal with filtration and not to complete oxidiation of organics to CO_2 since extended contact times and very high dosages is needed for this transformation (Constantine, 1982). The removal of organic matter removal with ozonation and adsorption on activated carbon needs to be measured by determining the DOC.

Correlation between colour removal with alum and ferric chloride

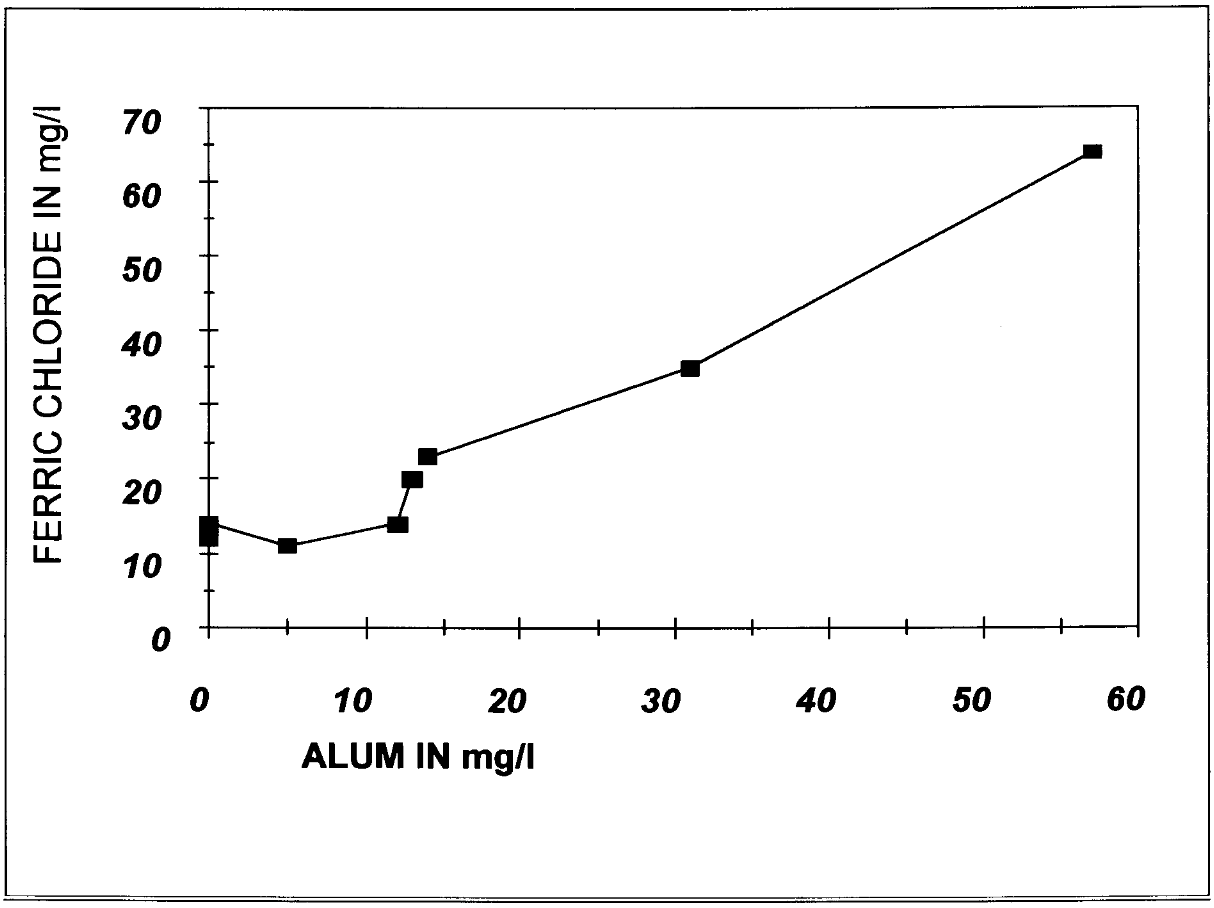


Figure 5: Correlation of colour removal by ferric chloride and alum

Mixing intensity

For effective coagulation on bench scale and in practice, two mixing stages are required. Rapid mix enables the distribution of coagulant throughout the water. The slow mix enables floc growth. When the predominant mechanism of coagulation is adsorption-destabilisation, occurring at low pH, the rapid mix intensity (Healy *et al.*, 1987) will affect effectiveness of coagulation and removal. The time required for destabilisation is in the order of a fraction of a second (Letterman *et al.*, 1973) and inefficient mixing may lead to restabilisation in some areas and insufficient destabilisation in others. Floc strength is also dependant on the energy input Tambo and Hozumi, 1979) at the rapid mixing. Floc size distributions also were more favourable for settling at high mixing intensities (Leu and Ghosh, 1988). Slow mixing times was found not to influence organics removal (Semmens and Field, 1980).

Early theories of flocculation kinetics were developed by Von Smuluchowski and Camp (Tambo and Wantanabe, 1979) and proposed the mean velocity gradient G and Gt (t=time) values as criteria for desgn of coagulating systems. The effective Gt values for rapid mixing should be reported in coagulation studies in order to design for optimu conditions on the plant. The optimum Gt value for polymers are generally given at 100000 (Tambo and Hozumi, 1979).

Jar stirrer aparratus are commonly used (Semmens and Field, 1980) for evaluation of coagulation efficiency. In order to determine Gt obtained in a jar stirrer the system should be characterised. Round glass beakers stirred with flat paddles often form vortexes which limits attainable power input to the water and makes full-scale correlating difficult (Cornwell and Bishop, 1995). However, exponential relationships were defined for mean velocity gradients applicable to jar stirrers with a flat paddle using round one litre beakers by Botha (1995). Estimation of the approximate G-values achieved during the tests with round glass beakers was obtained for 800 ml of fluid in a tall one litre glass beaker: $G = 0.042N^{1.549}$ where N is the revolutions per minute.

Rapid mixing speed was tested for optimum colour removal. There was no difference in colour removal for speeds over 200 rpm. Colour removal was greatly enhanced, however, when the slow mixing speed (flocculation) was increased from the normal 20-30 rpm to 50 rpm (Figure 6) (Narkis and Rebhun, 1983, Weber and Jodellah, 1985). Flocculation time above 10 minutes was not critical for colour removal

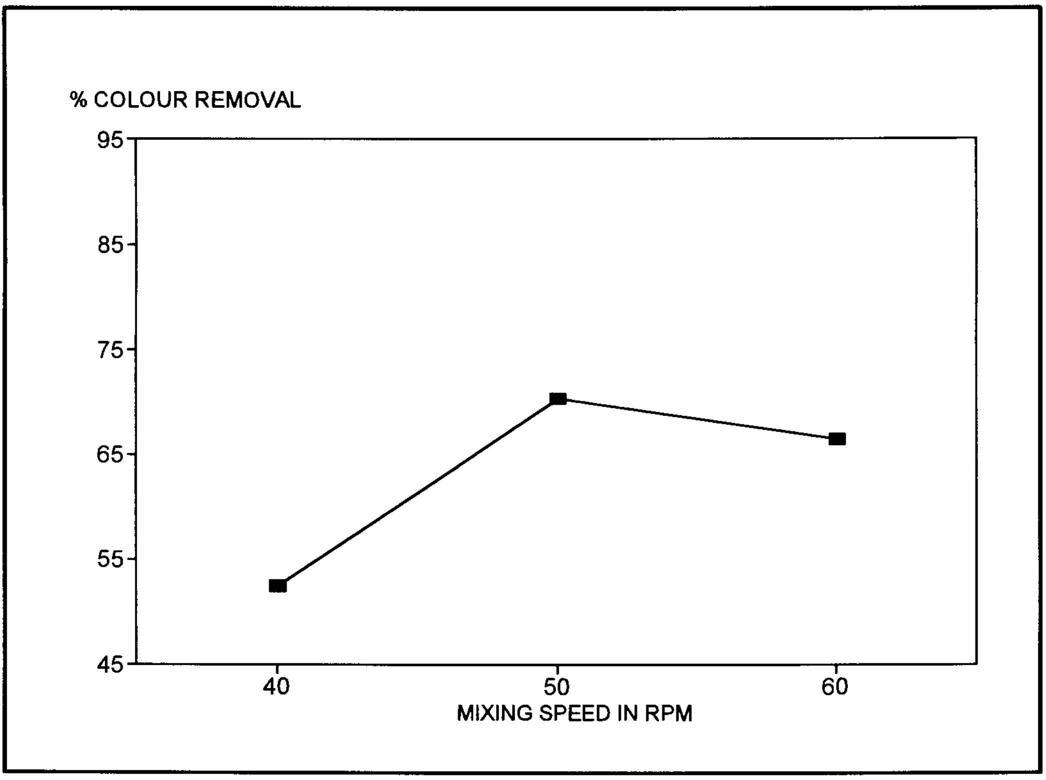


Figure 6 Influence of slow mixing speed on colour removal

Ozonation and turbidity

Turbidity removal was improved with pre-ozonation of secondary effluent. Ozonation after coagulation increased tubidity due to micro floc formation. This turbidity was easily removed with dosages of coagulant which would have been inefficient without ozonation Figure 7.

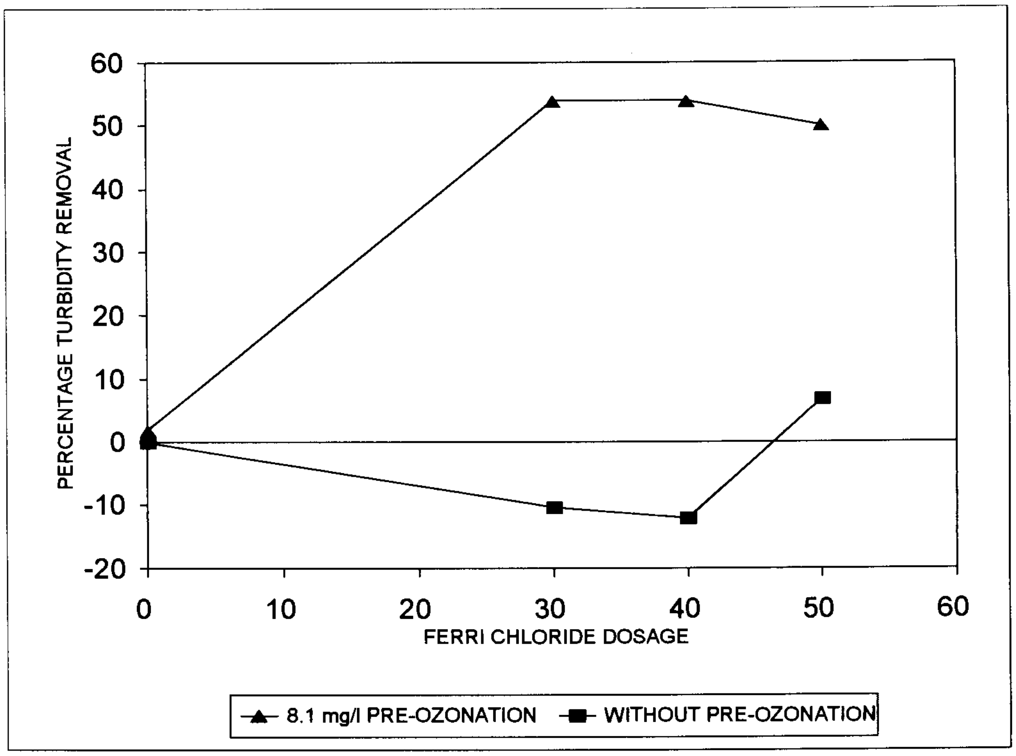


Figure 7: Comparison between removal of turbidity with coagulation with ferric chloirde before and after ozonation.

Breakpoint chlorination

Breakpoint chlorination of secondary effluent is shown in Figure 8.

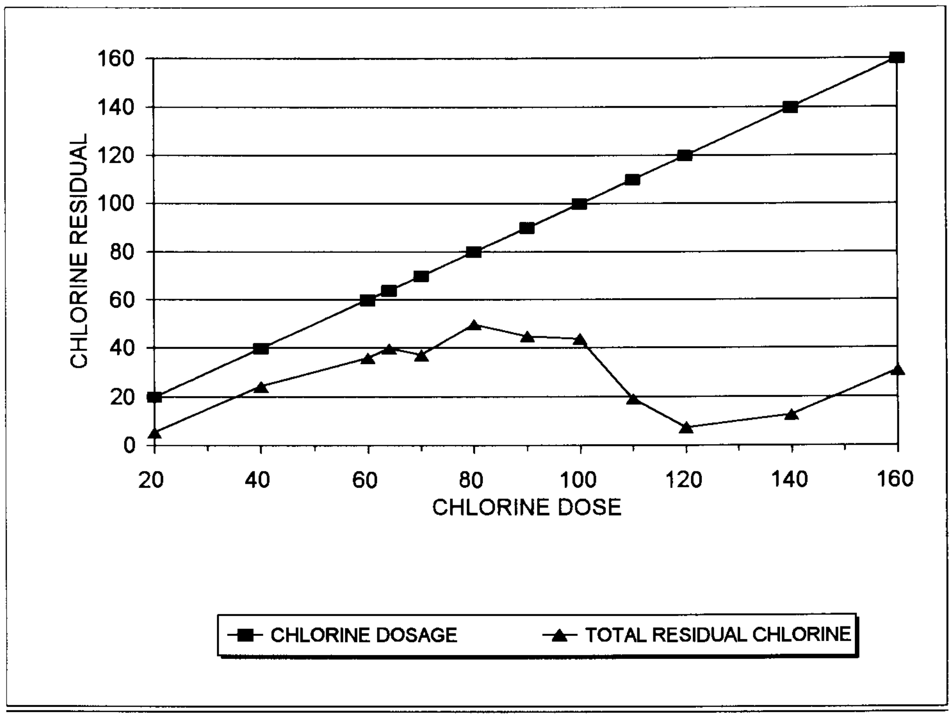


Figure 8: Breakpoint chlorination for secondary effluent

Breakpoint chlorination for water flocculated with 60 mg/l U3500 is shown in Figure 9

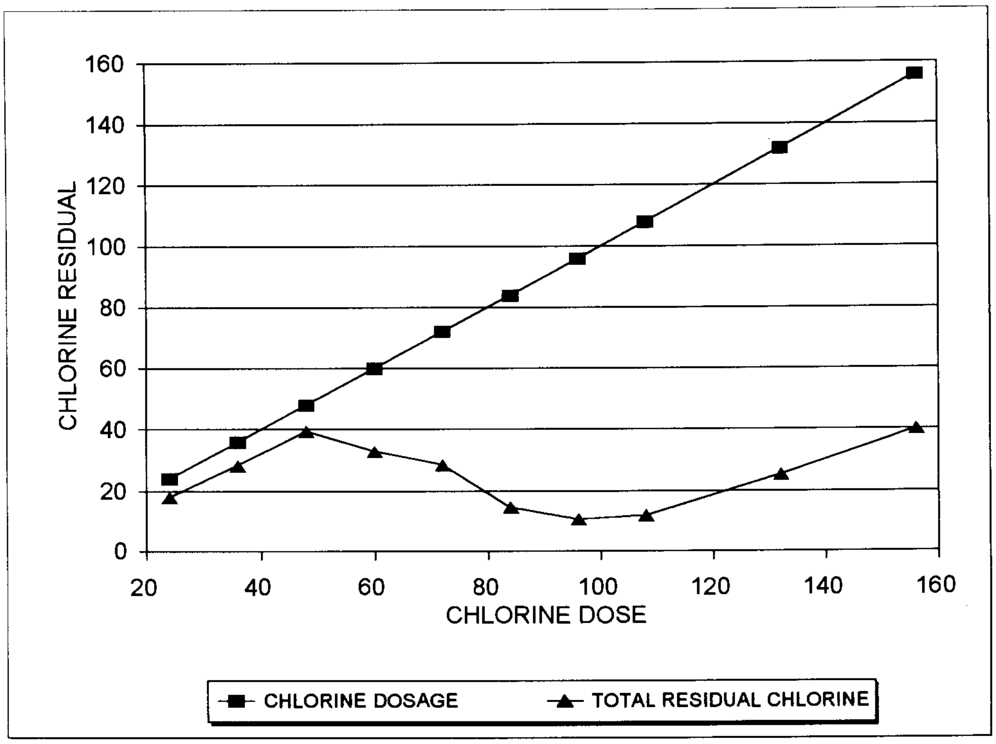


Figure 9: Breakpoint chlorination for secondary effluent coagulated with 60 mg/l U3500

Breakpoint chlorination of flocculated and ozonated water is shown in Figure 10

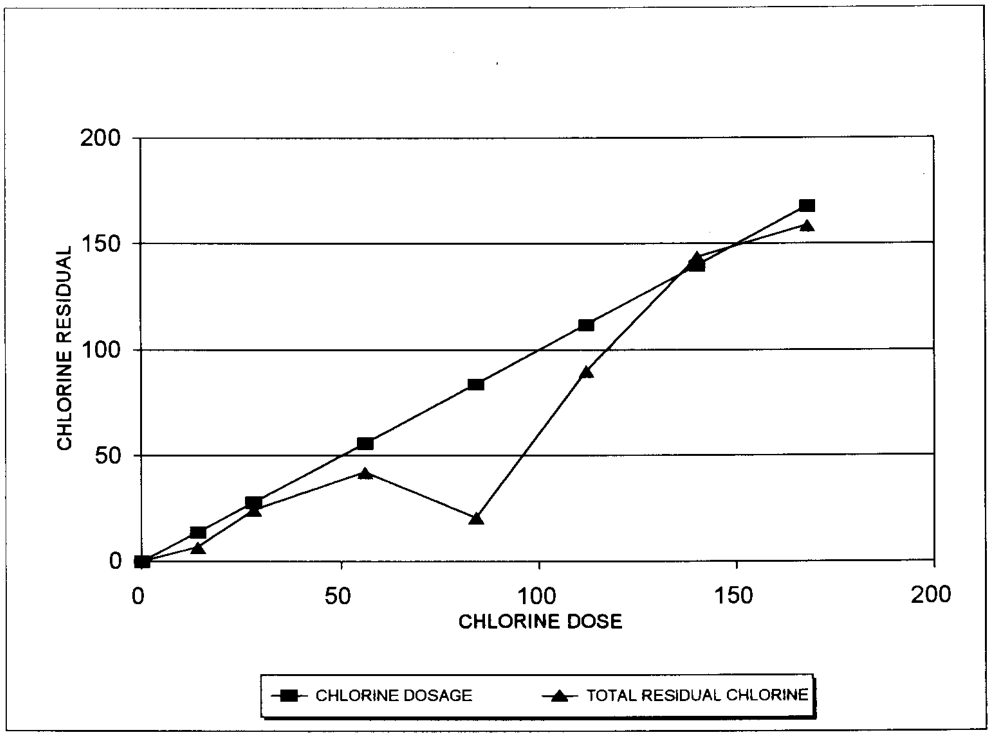


Figure 10: Breakpoint chlorination for secondary effluent coagulated with 60 mg/l U3500 and ozonated with 5.5 mg/l ozone.

APPENDIX 3: PLANT DESIGN AND RESULTS

A full scale effluent reclamation plant treating 1500 m^3/day was commissioned in January 1996 at the Johannesburg Abattoir. The process steps are coagulation, sedimentation, ozonation, sand filtration, activated carbon filtration and chlorination. A schematic diagram of the process is presented in Figure 1.

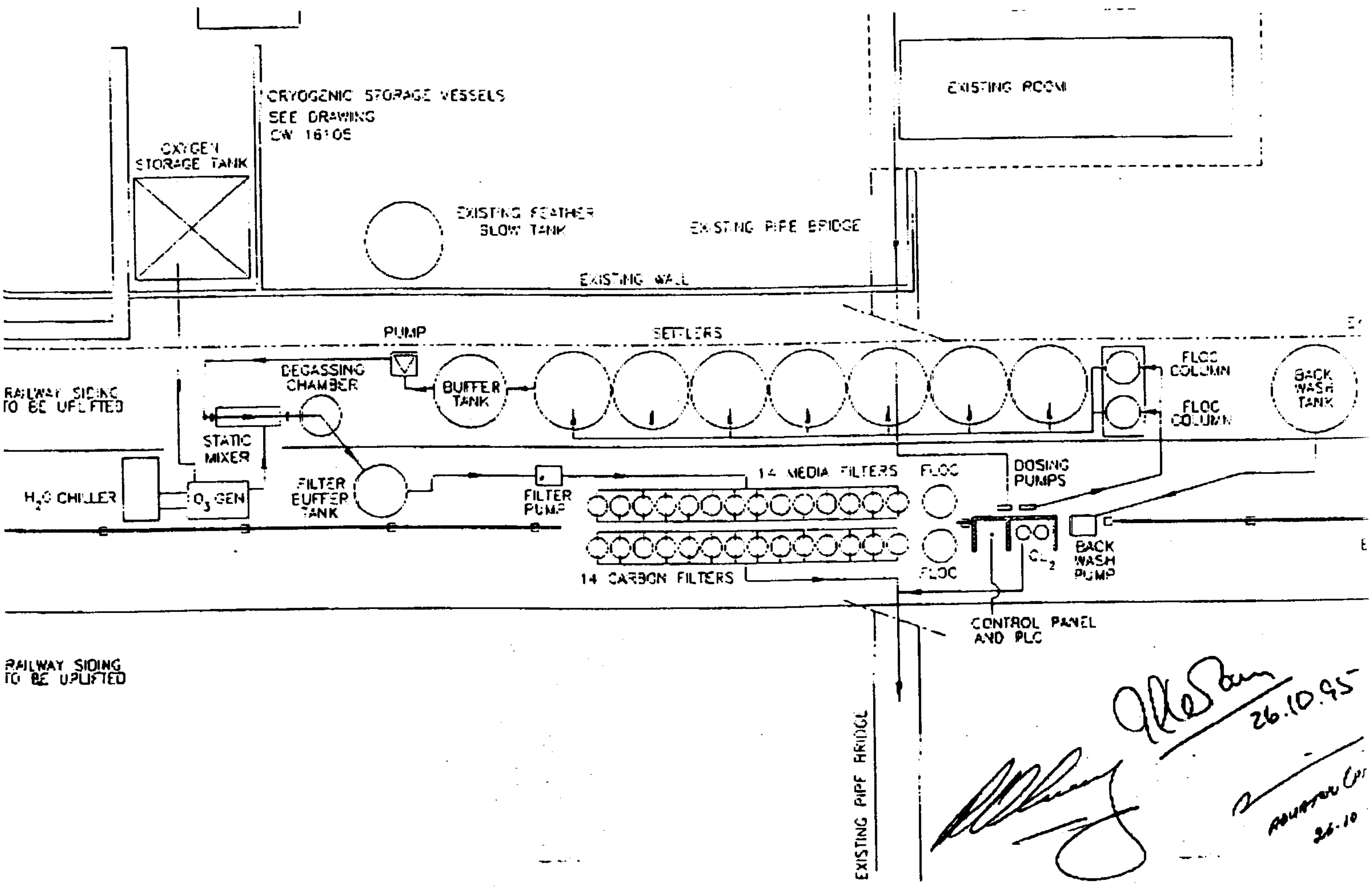


Figure 1. Process diagram of the full scale effluent reclamation plant at the Johannesburg Abattoir (Van Heerden, 1995)