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Report to the

WATER RESEARCH COMMISSION

on

GUIDELINES FOR THE USE OF PEROXONE AND OTHER OXIDANTS FOR THE TREATMENT OF EUTROPHIC AND COLOURED WATERS IN SOUTH AFRICA

by

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WRC Report No. 443/1/97
ISBN 1 86845 300 6

PRETORIA
November 1996

TABLE OF CONTENTS

EXECUTIVE SUMMARY

Interest in ozone as an alternative to chlorination has been on the rise in recent years. There are several reasons for this. First, the need for disinfection and oxidation of water is increasing as the population of municipalities grow and the volumes of municipal and industrial waste in the nearby rivers and lakes increase. Second, technological advances have included the creation of more and more chemical compounds, elements of which invariably appear in the influent waters of drinking water treatment plants. Third, it has come to light in recent years that chlorine based disinfectants, while providing disinfection, can combine with organic compounds to form materials which may present serious health hazards to humans and other life forms. Also, heavily chlorinated water has an associated taste, which most people find undesirable.

Ozone can react via two main ways which are a direct oxidation route which is usually very selective and an indirect oxidation by entities resulting from decomposition of ozone in water. Research has shown that the oxidising capacity of the ozonation process can be increased significantly by the addition of hydrogen peroxide. This process, known as PEROXONE, promotes the production of high-energy, short lived hydroxyl radicals (OH·) from the accelerated decomposition of ozone by hydrogen peroxide (The indirect oxidation route). The OH radical attacks organic compounds indiscriminately and can oxidise some of them to carbon dioxide and water. Effective oxidation appears to be greatly dependant upon the applied ozone dosage, the peroxide/ozone ratio, the contact time, and the composition of the raw water.

The objective of this project was to investigate the effectiveness of PEROXONE as a chemical oxidant on eutrophic and coloured waters. Comparative studies with ozone, hydrogen peroxide, chlorine, chlorine dioxide and ultra violet irradiation were also performed. More specific objectives of this study was to investigate the oxidation efficiencies of the above oxidants on colour removal, taste and odour removal and the effect of ozonation on flocculation/coagulation processes. A number of bench scale, pilot plant and full scale plant studies were undertaken in order to quantify the use of these oxidants for the removal of specific pollutants.

Generally it was found that colour removal was obtained via the direct ozone reaction. It was however seen that colour removal could be accomplished with hydroxyl radical oxidation, however not as effective as with ozone alone. Chlorine and chlorine dioxide could effectively remove colour whereas the use of hydrogen peroxide was ineffective in oxidizing humic and fulvic acids. It was also found that the presence of scavenging compounds such as carbonate ions had a detrimental impact on the radical oxidation process.

The oxidation of taste and odour compounds followed the radical oxidation pathway where the addition of hydrogen peroxide to ozone and UV led to enhanced removal of the compounds. In contrast to this, the use of conventional oxidants such as chlorine, chlorine dioxide and hydrogen peroxide were not effective in removal of these compounds.

In terms of trihalomethane formation, the use of ozone, PEROXONE and chlorine dioxide are preferable over the conventional use of chlorine. Ultra Violet Irradiation, although not cost effective for oxidation purposes, produces no or very little THM's

The difference in oxidation behaviour of phenol and DBS indicates that some prediction in whether a specific compound will be susceptible to radical pathway oxidation can be made. It is seen that where the direct oxidation reaction prevails (with phenol), the compound doesn't absorb UV light, is not removed with hydrogen peroxide and effective oxidation with chlorine and chlorine dioxide takes place at low and high pH values. This situation is reversed when the radical pathway oxidation mechanism is preferred. It is seen with DBS that the compound reacts favourably to UV irradiation and that hydrogen peroxide at high pH values oxidises the compound. In contrast with phenol, very little removal takes place when chlorine or chlorine dioxide is used at low pH values.

In general it was seen that ozone had no impact on improving flocculation.

The use of PEROXONE in potable water treatment has a niche position and must have a **specific objective** such as the removal of a taste and odour compound or a pesticide. The implementation of an advanced oxidation process is also dependent on the type of unit processes already installed in the treatment plant. If the treatment plant for example already employs the duty of an ozone plant or UV irradiation, the extra cost for dosing of hydrogen peroxide will be minimal.

The process must be also be **cost effective**. In order to perform a cost analysis it will be important to determine dosages required as well as true costs associated with the specific oxidant such as discussed in chapter 6. Dosage determination should be conducted under controlled conditions and on a typical water sample to be treated. It is important that the destruction of specific micropollutants should not be investigated in the absence of background natural organic material. Because these natural organic materials are often present at concentrations several orders of magnitude greater than the micropollutant of interest and because these radical reactions are nonselective, the effectiveness of these processes for destroying specific micropollutants in such a natural water matrix should be determined.

Attention must be given to the **health implications** associated with the use of that specific oxidant. It was seen that the use of ozone and PEROXONE produce very little if any THM's on its own, however the subsequent chlorination of the water can indeed form more THM's due to breakdown of organics into compounds susceptible to THM formation. The use of chlorine dioxide for oxidation of organics resulted in low dosages to be used, as well as low formation of THM's and looks favourable. Apart from THM formation, one should also be aware of the possible effects of bromate formation when ozone is used as oxidant and/or disinfectant. Although this issue is still debatable, it cannot be disregarded.

Although the use of UV and the combination thereof with hydrogen peroxide was also investigated, its commercial use can be limited due to the high dosages required. Where UV is normally used for disinfection purposes with dosages in the region of 40 mWs/cm^2, the dosages needed for oxidation is several orders of magnitude more; this leads to high treatment costs.

ACKNOWLEDGEMENTS

Thanks are due to the following members of the Steering Committee who guided the research ;

Chairman : Mr G Offringa - Water Research Commission
Secretary : Mr D Huyser - Water Research Commission
Members : Mrs N Basson - Goldfields Water
Mrs MJF Kruger - Western Transvaal Regional Water Company
Mr IA Pearson - Watertek - CSIR
Mr CD Swartz - Watertek - CSIR
Mr JC Geldenhuys - Rand Water
Mr M Pryor - Umgeni Water
Dr CF Schutte - University of Pretoria
Dr RH Reimann - Alliance Peroxide

The financial support of the Water Research Commission which sponsored the research studies is gratefully acknowledged.

Alliance Peroxide are thanked for providing hydrogen peroxide which were used in the laboratory-, pilot plant- and full scale studies.

Two colleagues at Watertek, CSIR, deserve special thanks for their work. These are Chris Swartz which assisted with the initial implementation and for general guidance, and Gideon Joubert who spent days away from home for executing the pilot plant and full scale studies.

I would also like to thank staff of the analytical laboratories at Watertek for their help with analyzing the numerous samples.

Finally, my appreciation is extended to GFJ Inc. who gave me the opportunity to complete this work when leaving the CSIR halfway through the project.

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1 : INTRODUCTION AND OBJECTIVES OF THE STUDY

1.1 Introduction

High-quality drinking water is one of the most precious commodities of all, and pure water is one of the basic necessities of life. An inadequate quality can lead to serious health problems for consumers. Chlorination has long been the most popular drinking water oxidant/disinfectant used in water treatment (Klein and Smith, 1989). Interest in ozone as an alternative to chlorination has been on the rise in recent years. There are several reasons for this. First, the need for disinfection and oxidation of water is increasing as the population of municipalities grow and the volumes of municipal and industrial waste in the nearby rivers and lakes increase. Second, technological advances have included the creation of more and more chemical compounds, elements of which invariably appear in the source waters of drinking water treatment plants. Third, it has come to light in recent years that chlorine based disinfectants, while providing disinfection, can combine with organic compounds to form materials which may present serious health hazards to humans and other life forms. Also, heavily chlorinated water has an associated taste, which most people find undesirable.

Ozone is a much more powerful disinfecting and oxidising agent than chlorine (Klein and Smith, 1989). Oxidation is a process by which compounds are broken down. The process is applied equally to microorganisms such as bacteria, in which cases the organisms are killed by a disinfectant first before the oxygen demand for the breakdown of their constituents are satisfied. Disinfection is a means of destroying pathogenic microorganisms, while oxidation is often key to the elimination of compounds which may be toxic or cause bad taste, odour or colour. Both chlorine and ozone fulfil each of the roles of disinfectant and oxidant; ozone can generally carry out either task several times faster than chlorine.

Ozone has been used continuously for the treatment of drinking water since 1906 when it was first installed in the city of Nice, France, for disinfection (Collins et al, 1989). Although many water treatment plants throughout the world still utilize ozone primarily for disinfection, newer facilities increasingly rely on ozone to perform one or more oxidation functions. Major purposes of ozone usage in treatment facilities include:

- bacterial disinfection and viral (and algal) inactivation;
- destruction of organic substances such as humic materials, pesticides, detergents, phenol, and residues of polymers used for treatment;
- destruction of trihalomethane (THM) precursors;

- aiding coagulation for waters containing organic substances;
- removal of colour, taste and odour;
- oxidation of soluble iron and manganese, also decomplexing of organically bound metals;
- oxidation of cyanide to cyanate and eventually to carbon dioxide and water; and
- partial oxidation of organics for subsequent biological degradation.

Selection of the appropriate ozone dosage for any of these operations is normally determined by pilot plant investigations. For many applications, excessive ozone dosing, although not economic, does not produce detrimental effects. However, this is not always the case. For example, high ozone dosages may lead to increased THM formation potential as simpler, more readily halogenated organic by-products are formed. The selection of a pre-ozonation dosage to maximise the benefits of the coagulation-flocculation process is also a situation where sufficient evidence exists to suggest an optimum ozone dosage should be selected (Collins et al, 1989).

With regard to reactivity, ozone can react via two main ways which are (Brunet et al, 1985):

- a direct oxidation by molecular oxidation, which is usually very selective; and
- an indirect oxidation by entities resulting from decomposition of ozone in water.

With regard to direct oxidation, it primarily affects unsaturated compounds such as ethylene, aromatic compounds and some other compounds with specific functional groups.

Research has shown that the oxidising capacity of the ozonation process can be increased significantly by the addition of hydrogen peroxide (Wolfe et al, 1989). This process, known as PEROXONE, promotes the production of high-energy, short lived hydroxyl radicals (OH·) from the accelerated decomposition of ozone by hydrogen peroxide. The OH radical attacks organic compounds indiscriminately and can oxidise some of them to carbon dioxide and water. Effective oxidation appears to be greatly dependant upon the applied ozone dosage, the peroxide/ozone ratio, the contact time, and the composition of the raw water.

The breakdown of ozone can also be catalyzed to enhance the production of OH radicals by placing ozone in a high-pH solution, combining UV light with ozone and combining H_2O_2 with UV light. Techniques that promote the formation of the free OH· radical are known as advanced oxidation processes (Glaze et al, 1987).

1.2 Objectives

The objective of this project was to investigate the effectiveness of PEROXONE as a chemical oxidant on eutrophic and coloured waters. Results obtained would be used to draw up guidelines for the use of PEROXONE and other oxidants for the treatment of eutrophic and coloured waters in South Africa. Comparative studies with ozone, hydrogen peroxide, chlorine, chlorine dioxide and ultra violet irradiation were performed.

More specific objectives of this study were to investigate the oxidation efficiencies of the above oxidants on colour removal, taste and odour removal and the effect of ozonation on flocculation/coagulation processes.

CHAPTER 2 : LITERATURE REVIEW

2.1 Production of the OH radical

2.1.1 Ozonation at high pH values

Hoigne and Bader (1976) showed that the mechanism of ozonation seemed to change at high pH values. The relative rate constants for high pH ozonation of pairs of organic compounds were found to be the same as those for reaction of the same compounds with hydroxyl radicals generated from radiolysis of water.

At higher pH values, there is however an important factor that works against the effectiveness of ozonation processes. Hoigne has pointed out that increasing the pH will not necessarily increase the rate of OH radical destruction of a substrate because of enhanced trapping effects. At pH values greater than 10.3, carbonate ion is a more prevalent species than bicarbonate ion, and the rate constant for the reaction of OH· with carbonate ion is over twenty times greater than with bicarbonate ion. The benefit of ozonating at high pH values should therefore be weighed against the scavenging effect of the carbonate ion.

2.1.2 Ozone with Hydrogen Peroxide

H_2O_2 initiates the decomposition of ozone resulting in the formation of hydroxyl radicals. Glaze et al, 1987, investigated the effect of different ratios of H_2O_2 to O_3 on the rate constant of oxidation of tetrachloroethylene (TCE) and found that the rate constant shows a hyperbolic dependence on peroxide with a maximum at a ratio of about one mole of peroxide per mole of ozone (0.7 mg H_2O_2/mg O_3). This is the function expected if peroxide acts as a promoter as well as an OH radical scavenger. It is indeed known that peroxide will act as an OH radical trap as well as an initiator. From the equation

$$H_2O_2 + OH\bullet - O_2^- + H_2O + H^+$$

it can be seen that the superoxide ion, O_2^-, is formed. Since this ion also promotes the decomposition of ozone, it is not clear why peroxide at high concentrations inhibits the advanced oxidation process.

2.1.3 Ozone with Ultraviolet Irradiation

The photolysis of ozone in wet air produces hydroxyl radicals by a two step process (Okabe, 1978) :

$$O_3 + h\nu\ (\lambda < 310\ \text{nm}) = O_2 + O$$
$$O + H_2O = OH\bullet + OH\bullet$$

Previously it was assumed that photolysis of ozone in water would proceed by a similar pathway; however Taube (1957) showed, and more recently Peyton and Glaze (1984, 1986) confirmed that this is not the case and that hydrogen peroxide is formed in the process.

$$O_3 + h\nu + H_2O = H_2O_2$$

It would therefore appear that the O_3/UV and O_3/H_2O_2 processes are one and the same; in the former, hydrogen peroxide is formed in situ, rather than adding it from an external source. For some substrates, that is the case and for other substrates which absorb ultraviolet radiation, the O_3/UV process can be much more. When a substance absorbs strongly in the UV region, large fluxes of UV irradiation will accelerate the destruction of the substance, for example aromatic halides (Glaze et al, 1987). On the other hand, when the substance of concern is not photolysed directly with much efficiency, the use of UV irradiation to generate hydrogen peroxide makes little sense. In such cases it is preferable to add hydrogen peroxide from an external source. Dosing of peroxide into a water stream is a trivial task compared to the use of UV lamps with problems such as clouding and flux decay.

2.1.4 Hydrogen Peroxide with Ultraviolet Irradiation

The most direct method for the generation of hydroxyl radicals is through cleavage of hydrogen peroxide. Photolysis of H_2O_2 is known to yield hydroxyl radicals by a direct process i.e. with a quantum yield of two OH radicals formed per quantum of radiation adsorbed (Glaze et al, 1987) :

$$H_2O_2 + h\nu = OH\bullet + OH\bullet$$

In order to generate a sufficient level of OH radicals, a high concentration of H_2O_2 is required.

2.2 Oxidation of Organics

Ozone acts first as an oxidizing agent, then as a disinfectant. It does not produce irritants in the water, but does not produce a lasting residual (Mood, 1989). It is therefore still necessary to add a disinfectant which provides a residual for protection of the consumer. After ozone has done the oxidizing and main disinfection task, however, the demand for a secondary disinfectant is much smaller and if chlorine is to be used, the negative effects will be alleviated to a large extent.

More than 700 organic compounds have been identified in drinking water, however, not all of these materials are oxidized by ozone at the same rate (Kirk-Othmer, 1981). Ozone can react with natural organic material directly as molecular ozone (O_3) or via an indirect pathway in which free radicals such as OH· and HO_2· serve as the oxidizing agents (Chang and Singer, 1991). The direct pathway is very selective and organics such as phenols, olefins and simple amines react quickly with molecular ozone. Conversely, the indirect pathway is nonselective and tends to be faster than the direct pathway for many organic compounds. Organic contaminants that are slow to react with ozone, such as aldehydes and ketones are more likely to react via the nonselective free radical pathway.

In natural waters, it appears that the radical pathway dominates in oxidation reactions involving ozone and natural organic material (Chang and Singer, 1991). However, the indirect pathway can be significantly affected by pH and the presence of high concentrations of carbonate and bicarbonate that behave as free radical scavengers. These constituents can shift the reaction towards the direct ozone pathway.

Ozonation can lead to important modifications in the characteristics of organic material in natural waters. Ozonated humic material has been reported to be more polar and of lower molecular weight than the parent material (Anderson et al, 1986).

2.2.1 Control of Trihalomethanes

Trace amounts of organic materials remain in treated water and react chemically with chlorine to produce trihalomethanes (THM's). These compounds may be carcinogenic and can create a potential health risk (Kirk-Othmer, 1981).

The control of trihalomethanes can be effected by one of three mechanisms :

- removal of the THM's after they are formed;
- removal of dissolved organics in the water prior to disinfection; or
- avoid using chlorine as a disinfectant.

Because ozone very quickly decomposes to oxygen, ozone cannot act as residual disinfectant, that is why chlorine is in many cases used as a residual disinfectant.

It is technically feasible to remove THM's by adsorption onto granular activated carbon (GAC). Different dissolved organic materials have differing adsorption efficiencies onto GAC, however, THM's have a relatively low adsorption efficiency on GAC. Therefore, a very high operating cost is associated with GAC adsorption as the carbon must be either replaced or regenerated frequently. Removing THM's by direct oxidation with ozone also is not possible because trihalomethane concentrations of less than 1 mg/ℓ in water do not exhibit any chemical reactivity with ozone (Kirk-Othmer, 1981). THM's are low molecular weight volatile compounds which lend themselves to air stripping, therefore, some reductions can be achieved by air-stripping (Myers, 1991).

Trihalomethane precursors can more effectively be removed by adding ozone at the front of the treatment plant to aid in the coagulation and subsequent removal of the precursors. Ozone can also be added as one of the last unit processes (say after sand filtration), so that it oxidizes any remaining THM precursors, but caution must be exercised when high concentrations of organics remain in the water. Partial oxidation of high concentrations of organics may alter their structure such that they produce more THM's upon subsequent chlorination. An effective method for the removal of THM precursors is ozonation followed by adsorption onto activated carbon in the presence of bacteria (Kirk-Othmer, 1981). The use of ozone in combination with GAC has a synergistic effect, because it allows more dissolved organic or THM precursors to be removed than would be removed by ozone or GAC alone. The economics of the process are attractive as well because GAC is continuously regenerated by the biological action of the surface of the carbon.

2.2.2 Removal of Colour

It is well known that naturally occurring colour is often caused by humic substances (Sierka et al,1989). Aquatic humic substances account for approximately 50 % of the dissolved organic carbon (DOC) present in most natural waters. The molecular weight distribution of aquatic humic and fulvic acids ranges from approximately 500 to 10 000. The stability of humic and fulvic acid molecules in water is largely due to a charge density imparted by acidic functional groups. These compounds result from the decay of vegetative materials and usually are related to condensation products of phenol-like compounds. Such colour-causing compounds include numerous conjugated double bonds which are readily split by ozone oxidation. Cleavage of only one double bond generally destroys the chromophoric properties of the molecule (that is the property that gives colour to the molecule). Humic/fulvic acid molecules can be removed by processes such as chemical coagulation and activated carbon adsorption (Singer et al, 1989). Low molecular weight (< 1000) fulvic acids are very hydrophillic (tends to stay dissolved in water - liquid loving) and not amenable to removal by coagulation or adsorption. Such a source becomes a candidate for an oxidative technique that can create partial oxidation products that are characterized by less colour. It should be noted that, while chlorine is an effective agent for decolorizing water, it is this reaction between chlorine and colour causing organic materials that is responsible for the production of some of the trihalomethanes (THMs) found in water.

In a case study by Singer et al (1989), the effect of ozonation on lake water for potable water purposes was investigated. This lake water was rich in humic substances and the colour averaged about 100 colour units. While the monthly average colour of the finished water (after flocculation, settling, filtration) was typically 3 to 6 colour units using chlorination, significant variability in the colour of the finished water on a daily basis was experienced. After adopting ozonation, colour removal was more consistent, and colour values less than 4 colour units were readily achieved.

2.2.3 Removal of Taste and Odour

Among the several tastes and odours present in drinking water, the most frequently encountered are those which are earthy and musty (Anselme et al, 1988). Many compounds can be the source of such tastes and odours, among them geosmin and 2-methylisoborneol (MIB) which are produced by living algae. A study by Lalezary et al (1986) has shown that oxidation of geosmin and MIB by chlorine, chlorine dioxide or potassium permanganate is not very efficient. Conflicting results concerning their removal by ozone have been reported in the literature. Experiments performed in pure water have shown that even with large ozone dosages over a 10 minute contact time, geosmin and MIB removal efficiencies are less than 50 % (Lalezary et al, 1986). On the other hand previous studies have reported a greater ozonation efficiency. Tatsumie (1987) has carried out a pilot plant study on the Yodo river water and the treatment process included sedimentation and ozonation at 2 mg O_3/ℓ. Under these conditions, the geosmin and MIB removal was found to be between 85 and 100 %. Yasutake, (1987) in a pilot plant study conducted on the Kasumigaura lake water, has shown that the MIB removal reached between 80 and 90 % and geosmin removal was close to 100 % by using an applied ozone dosage of 5 mg/ℓ over a 10 - 20 minute contact time.

These conflicting results may be explained by difference in water quality. Hoigne (1976) has shown that in water, ozone reacts following two different pathways : a direct reaction with molecular ozone and an indirect reaction of hydroxyl radical. Geosmin and MIB, which are tertiary alcohols, are non reactive towards molecular ozone but can be removed by hydroxyl radical formed during the ozone decomposition in water. Therefore, parameters such as pH and bicarbonate content have an influence on the hydroxyl radical production and scavenging, and variations in these parameters may explain the differences observed in the conclusions reported previously.

Duguet (1989) found that Geosmin and MIB are removed by ozonation. At pH 5,6 and 7,5, the concentration of geosmin is reduced from 350 - 500 ng/ℓ to around 100 ng/ℓ in 30 minutes. At pH 11, the reaction rate is 5 - 6 fold faster than at pH 5,6 and 7,5 , so the geosmin is reduced to less than 10 ng/ℓ with 20 minutes ozonation time. Similar results were obtained with MIB. As the removal of these compounds is due to the formation of hydroxyl radicals during ozone decomposition, the higher removal rate observed at pH 11 can be explained by the higher rate of ozone decomposition at basic pH, producing a higher hydroxyl radical flux.

In order to evaluate if hydroxyl radicals may participate to the geosmin removal, tests were performed by adding a scavenger which reacts rapidly with hydroxyl radicals reducing the amount of hydroxyl radicals available for geosmin oxidation (Duguet, 1989). The scavenger used for this study was tertio-butylalcohol. It was found that the presence of the scavenger at a 100 mg/ℓ concentration reduced the rate of geosmin removal by a factor 4 suggesting that geosmin is removed following a radical type reaction pathway. For these results it can be expected that systems such as ozone/hydrogen peroxide which produce hydroxyl radicals can enhance the removal rate of such compounds.

In a study by Duguet (1989) where hydrogen peroxide was used with ozone it was found that the removal rate of geosmin increased drastically, so it is possible to reach a geosmin concentration below 10 ng/ℓ in less than 5 minutes of ozonation time. The increase of hydrogen peroxide concentration had no influence on the removal rate.

Ferguson et al (1990) studied the use of PEROXONE for the removal of taste and odour compounds and he found that PEROXONE was significantly more effective in oxidizing the taste and odour compounds, MIB and geosmin, than was ozone alone. MIB removals of 90 % required an applied ozone dosage of 4 mg/ℓ compared with an ozone dosage of approximately 2 mg/ℓ for PEROXONE (0,2 $H_2O_2 : O_3$ ratio). The optimal ratio appeared to be 0,3 - 0,5. Oxidation of taste and odour compounds also appeared to be independent of contact time over the range studied (6 - 12 minutes).

In a study by Daniel and Meyerhofer (1989) it was found that :

- Geosmin is more readily oxidized than MIB;
- Ozone and ozone-hydrogen peroxide provide superior removal of geosmin and MIB when compared to other oxidants;
- The ranking in terms of effectiveness for geosmin removal is from greatest to least : O_3-H_2O_2 > O_3 > H_2O_2 > Cl_2 > $KMnO_4$;
- For MIB-removal, the trend is similar : O_3-H_2O_2 > O_3 > Cl_2 > $KMnO_4$ > H_2O_2;

2.3 Effect on Coagulation/Flocculation

In this field of ozone, numerous work have been reported in literature (Paillard et al,1989) either on the spontaneous flocculation in ozonated water (called the "microflocculation") or on the improvement of subsequent flocculation-clarification.

Reckhow et al (1986) summarized work reported in the literature providing a compendium of the five mechanisms most probably responsible for the observed beneficial effects of ozonation on coagulation-flocculation processes :

Mechanism 1 :	Increasing organic oxygenated functional groups, especially carboxylic, leading to increased complexation (primarily with calcium and alumina), and adsorption (to alum flocs).
Mechanism 2 :	Decreased molecular weight of dissolved organic carbon leading to reduced steric stability of organically coated particulates. The

repulsive energy between the particles is therefore decreased.

Mechanism 3 : Formation of meta-stable organics (e.g. ozonides, organic peroxides, and organic free radicals) that contribute to polymerization of organic material in a manner similar to the addition of a conventional polymer. It therefore aid in rapid floc formation and in creating heavier floc particles.

Mechanism 4 : Organo-metal complexes may be ruptured leading to the action of the liberated metals as conventional coagulants. These trivalent aluminium or ferric ions can then destabilize colloids by adsorption and floc enmeshment.

Mechanism 5 : Biopolymers may be liberated by the lysing of algae and could then act as conventional polymers.

Of the preceding mechanisms, the fourth and fifth are the most speculative and least supported in the literature. The rupturing of organo-metal complexes may liberate metals, which could subsequently be oxidized if not already, but at the same time smaller, more polar organic fragments would probably be found. These organic fragments are often more difficult to coagulate with metal coagulants than the original humics.

A study by Edwards and Benjamin (1991) investigated the effects of ozone on several water quality parameters that affect particle behaviour in water treatment systems. Among the results were those indicating what ozone did not do. Ozone did not decrease the critical coagulant concentration (the coagulant dosage required to bring the average particle zeta potential to 0 ± 1 mV) for $AlCl_3$, $FeCl_3$ or alum coagulants; destabilize particles or improve particle removal particle processes if pH was held constant. There was no evidence that disruption or desorption of the organic coatings of particles occurred, or, if it did, that it enhanced particle destabilization. pH decreases resulting from ozonation can improve particle removal by causing the surface potential of charged particles to become less negative and thereby improving the efficiency of metal salt coagulants. pH decreases during ozonation are favoured by low dissolved CO_2, high CO_2 concentrations in the ozone carrier gas, high total organic carbon in the solution, high solution pH, and high ozone dosages. The production of acid from reactions between ozone and organic matter increases at higher pH. In this study , decreases in pH substantially improved the efficiency of metal salts coagulants. Similar improvements were observed when solution pH was altered upon ozonation. Increases in solution pH during ozonation led to increased coagulant requirements.

It is well known that the effectiveness of coagulants is a function of pH. This is due to the formation of hydrolysis products which forms in certain pH ranges. It is therefore suggested that the effect of ozone on flocculation takes place rather via pH adjustment (albeit how small) than the mechanisms described above.

2.4 Health aspects of by-products of ozonation

Knowledge of ozone chemistry and reaction pathways with various organic species suggests that reaction products would include such compounds such as aldehydes, ketones, carboxylic acids and other aliphatic and hydroxylated aromatic forms. With the exception of the aldehydes, most of these do not appear to be detrimental to human health at the concentrations expected in ozonated drinking water. However, many of the studies conducted to characterize ozonation by-products have been performed at O_3-to-C weight ratios appreciably greater than 1 (Wilburn, 1993). For this reason, extrapolation of these observations to water treatment conditions is uncertain. At the Ozone-to-TOC ratios employed in drinking water treatment practice, most of the oxidized organic material is still likely to be macro-molecular in nature, although more polar and of lower molecular size than the parent material. The health effects of these by-products should be investigated.

2.4.1 Toxicity of bromate in drinking water

Considerable work has been done to date on the ingestion of potassium bromate. Listed below are a few finding with respect to this work : (Wilburn, 1993)

- Dose respond studies were made on rats over a 110 week period during which varying concentrations of bromate at between 0 and 500 mg/ℓ were consumed. It was found that definite carcinogenic effects were observed and that the effects were more significant in male animals.
- In a study on Syrian golden hamsters, positive effects were observed on the kidneys at $KBrO_3$ concentrations higher than 250 mg/ℓ.
- As conflicting observation can be mentioned that with mice given 0, 500 and 1000 mg/ℓ potassium bromate in drinking water for 78 weeks, in normal diet, no potential carcinogenic effect was observed.
- In acute toxicity studies, after oral dosage of 300 - 400 mg/kg on rats, more than 95% disappeared in the stomach after 30-60 minutes.

Until now, no conclusive mechanism could be formulated for the specific development of preneoplastic lesions in the kidneys by administration of bromate through the drinking water route in the diet of test animals (Masschelein, 1993).

The resistance of mice in the tests is surprising vs. the sensitivity of rats. Taking the lower limits of observation thusfar obtained as a preliminary basis, at least 60 mg/ℓ of bromate ion is the tolerable limit in drinking water if this is the only source of bromate in the diet. Bromate is the disinfection byproduct of the ozonation of bromide containing waters. The molecular ozone mechanism for bromate (BrO_3^-) formation includes bromide and ammonia concentrations and the pH as decisive control factors (Haag and Hoigne, 1983). The first product of the interaction of molecular ozone with bromide is hypobromide (OBr^-). This rapidly builds up during ozonation and becomes the main reservoir for bromide species. Hypobromite reacts with further ozone to form bromide (77%) and bromate (23%). In the usual pH range of drinking water treatment $[HOBr^-]_{tot}$ is predominantly present as hypobromic acid. Because $HOBr^-$ is only very slowly oxidized with ozone, the pH is the main control factor for bromate formation.

The molecular ozone mechanism does not account for hydroxyl radicals always formed as secondary oxidants from decomposed ozone during water treatment (von Gunten _et_ _al_, 1993). OH radicals lead to the formation of BrO radicals through several pathways. These undergo a disproportionation to hypobromite and bromite ($2BrO + H_2O = BrO^- + BrO_2^- + 2H^+$). Bromate is then formed through oxidation of bromite by ozone. The OH radical mechanism for the formation of bromate thus includes two decisive reaction steps, still being due to molecular ozone.

The importance of the bromate problem is tied directly to the particular standard adopted by the different health organizations. One value of 25 µg/ℓ would only cause minimal problems for some utilities, whereas at a value of 10 µg/ℓ, changes ranging from a simple adjustment of the oxidation processes to a complete modification of the process train could be required. A value of several micrograms per litre or less would throw back into question the use of oxidation processes, as much as for chlorine as for ozone. The optimization of a process for minimizing bromate formation can therefore be incompatible with other objectives in water quality (Mallevialle, 1993).

CHAPTER 3 : LABORATORY STUDIES

Ozonation was performed in a bubble column reactor with a volume of 450 mℓ. Deionized water spiked with a specific organic compound was used. Two containers with potassium iodide (KI) solution were used to monitor the amount of ozone not reacting with the organic compound, thereby enabling one to determine the exact dosage that was required to oxidize the organic compound. This experimental setup is shown in Figure 3.1. Oxidation by Clorine, ClO_2 and H_2O_2 was performed in a continuous stirred tank reactor with a volume of one litre. Oxidation by UV and UV/H_2O_2 took place in a UV generator/reactor. This reactor has a volume of 1.5 ℓ and was used as a batch reactor. For the combination of O_3/UV oxidation, the UV reactor was turned vertically to act as a bubble column while ozone was introduced through a diffusor at the bottom.

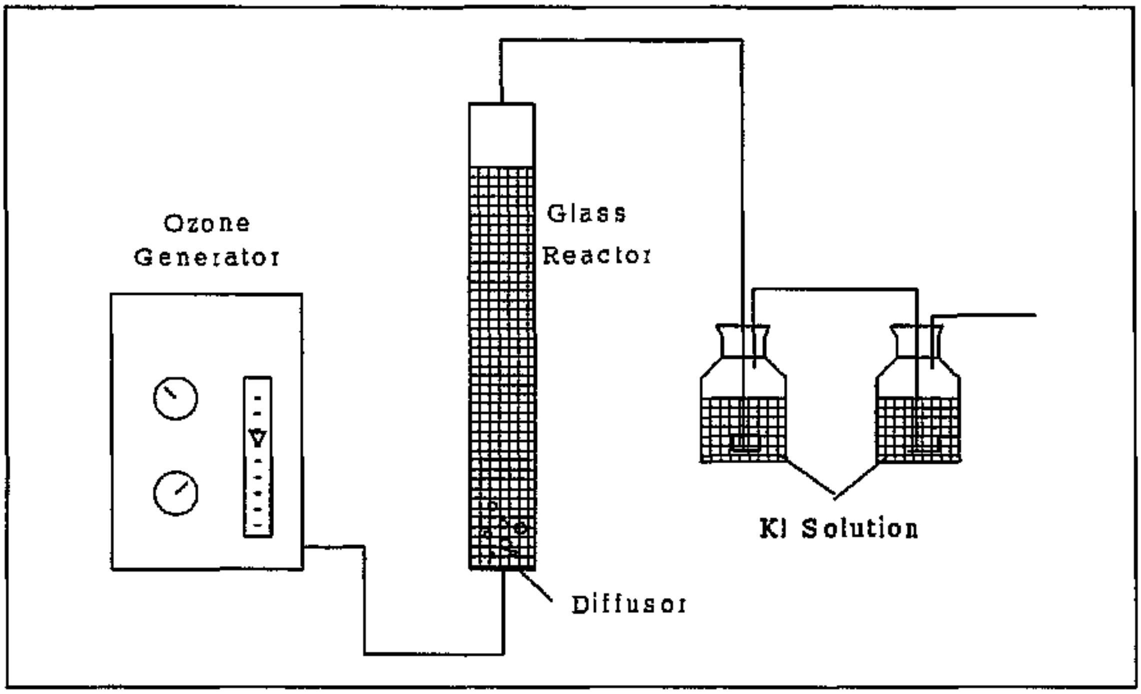


Figure 3.1 : Experimental setup

The organic compounds that were tested are phenol, dodecyl-benzene-sulphonate (DBS), humic acid (causing a brown colour to the water), and geosmin and 2-methyl-iso-borneol (Two taste and odour imparting substances in water).

Colour analyses were done on a DR/700 Colorimeter, Phenol determination by high pressure liquid chromatography, DBS measured by ion association with crystal violet dye and extraction of the ion-pair complex into benzene and Geosmin and MIB concentrations determined by closed loop stripping analyses (a GC-MS method).

Trihalomethane formation potential is determined by the addition of 12 mg/ℓ of chlorine to allow trihalomethane formation. THM analyses were done according to the procedure outlined by van Rensburg and Hassett (1982). The chlorinated organics were concentrated by liquid extraction into 53% di-isopropyl ether and 47% hexane. Gas chromatographic separations occurred in a fused silica capillary column, and detection was by electron capture detector.

3.1 Oxidation of Phenol

Phenol is a white, crystalline compound and is of particular significance as it is toxic to marine life, creates an oxygen demand in receiving waters, imparts a taste to drinking water and can be carcinogenic to humans. The recommended maximum limit in South-African drinking water is 5 µg/ℓ (SABS, 1984).

Deionized water was spiked with phenol to a concentration of 3 mg/ℓ. (A rather high value was chosen to eliminate possible errors due to inaccuracies in the analytical methods at low concentration.) The water was ozonated at different pH levels to determine the effect of pH on the oxidation of phenol. One minute contact time equalled the addition of 5 mg/ℓ of ozone. It can be seen from Figure 3.2 that almost no oxidation of phenol took place at the acidic pH value of 4, while slightly better removal of phenol took place at the alkaline pH value than at neutral pH.

The effect of PEROXONE on the removal of phenol was investigated at three pH values with a H_2O_2/O_3 mass ratio of 0,4. The result of this is shown in Figure 3.3 where it can be seen that oxidation by PEROXONE follows more or less the same pattern as with ozone oxidation. It can however be seen from Figure 3.4 that ozone is more effective than PEROXONE for oxidation of this organic compound. This suggests that this compound is oxidised by the direct pathway reaction. Figure 3.5 shows the oxidation effect of using O_3/UV as an oxidant at the three selected pH values and results are comparable to those obtained by PEROXONE oxidation.

Figures 3.6 and 3.7 shows the oxidation of phenol with chlorine and ClO_2.

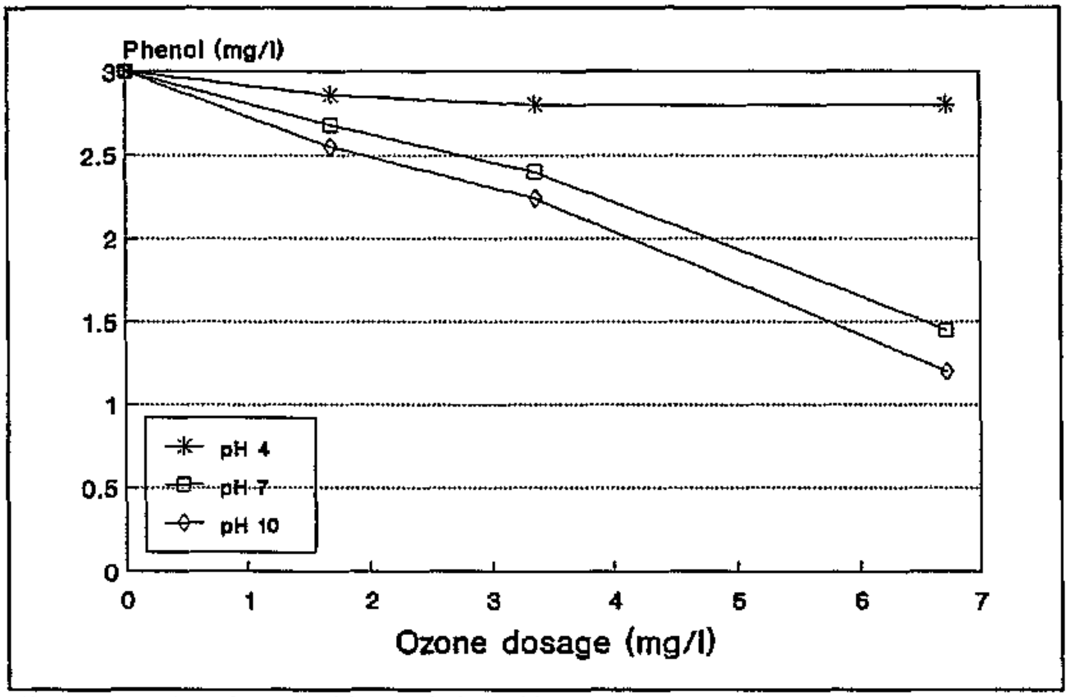


Figure 3.2 : Phenol removal by oxidation with ozone

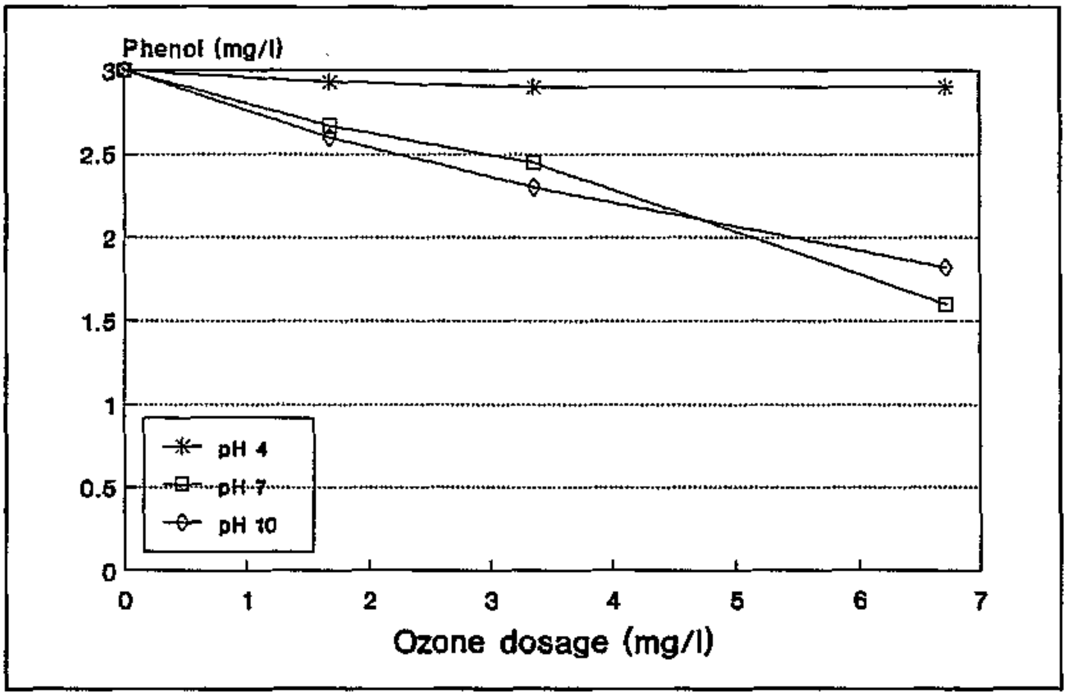


Figure 3.3 : Phenol removal by oxidation with PEROXONE

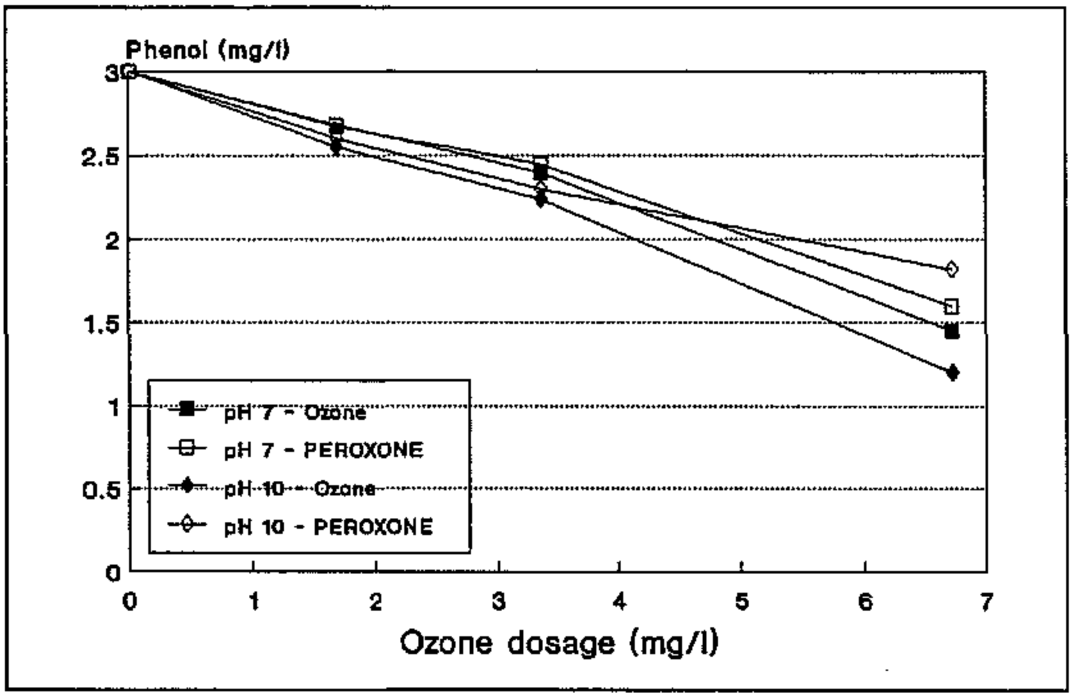


Figure 3.4 : Comparison of phenol removal with ozone and PEROXONE

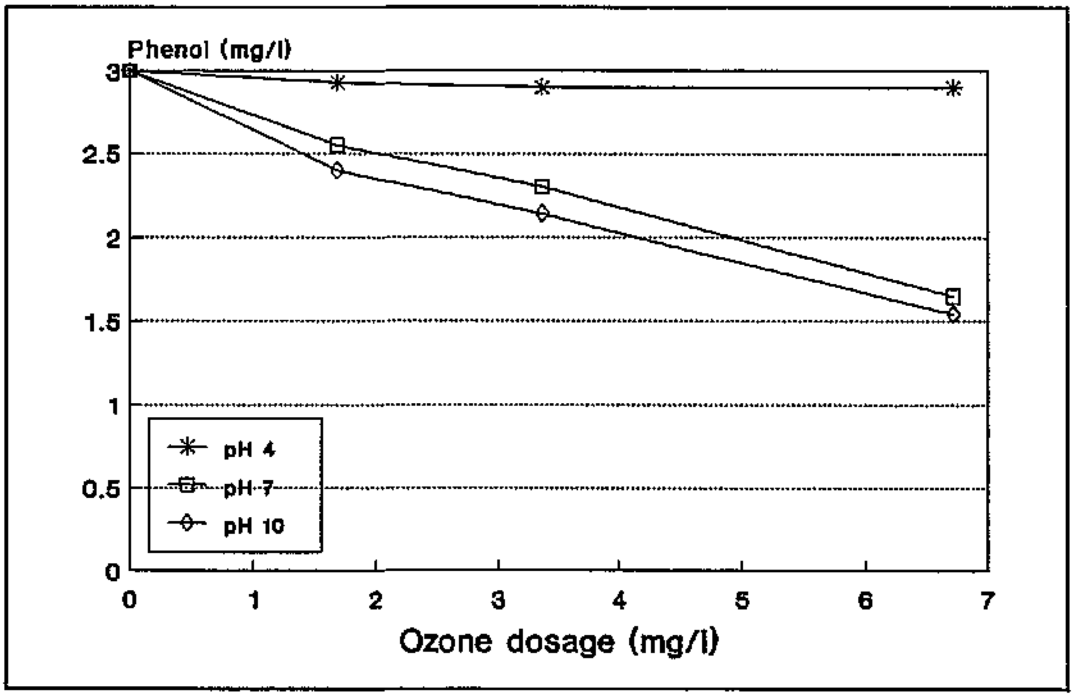


Figure 3.5 : Phenol removal by oxidation with UV/O_3

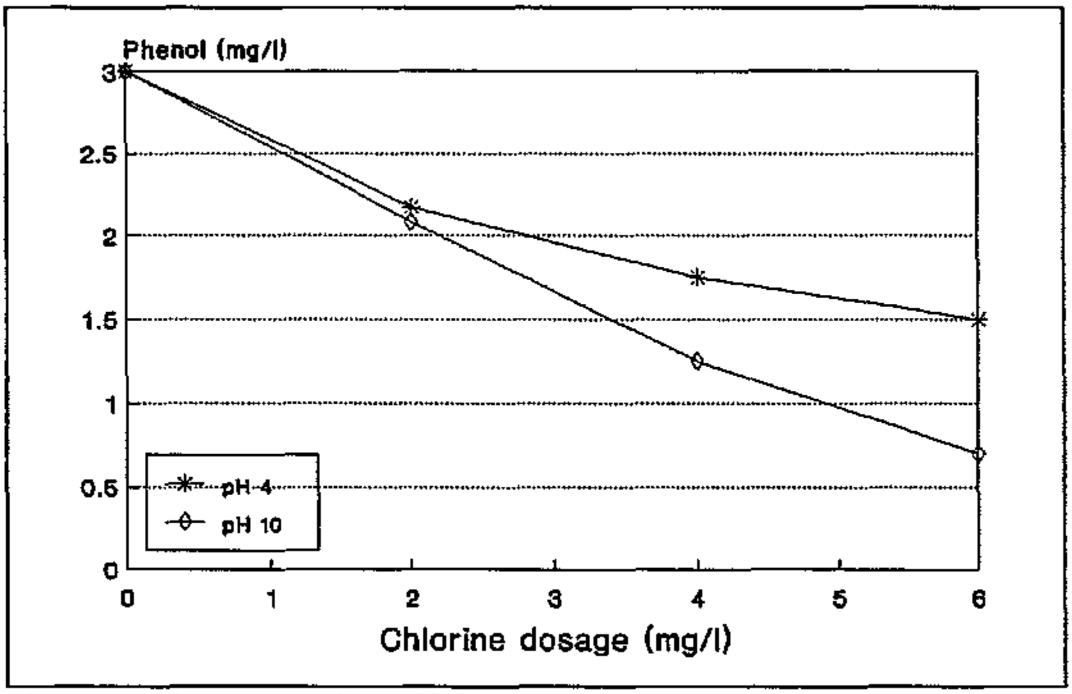


Figure 3.6 : Phenol removal by oxidation with chlorine

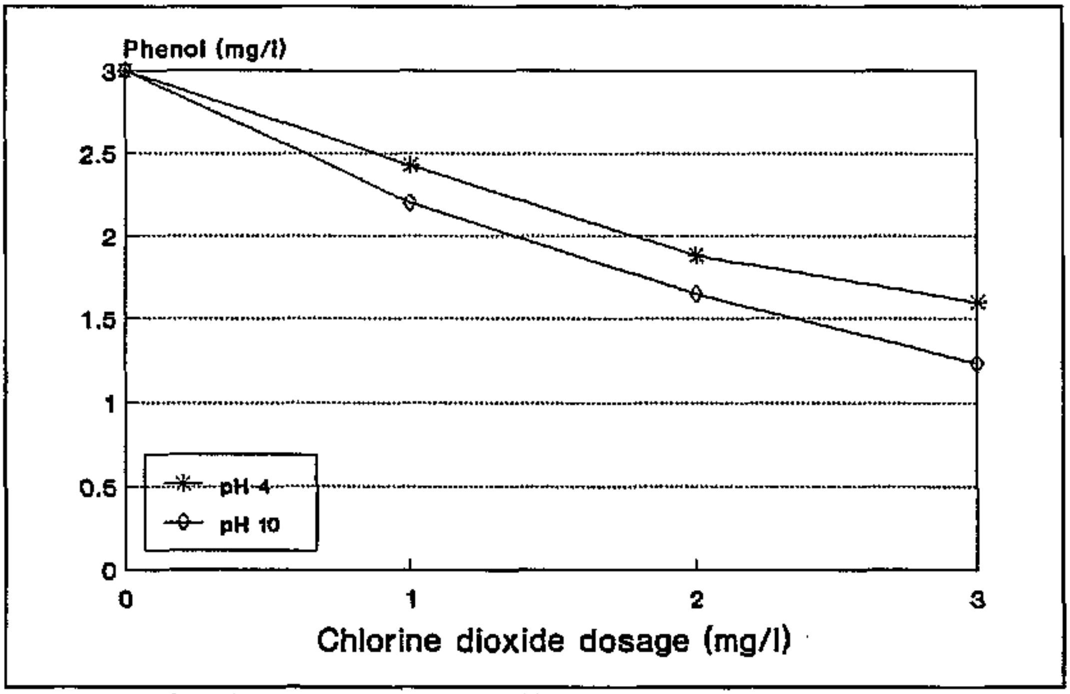


Figure 3.7 : Phenol removal by oxidation with chlorine dioxide

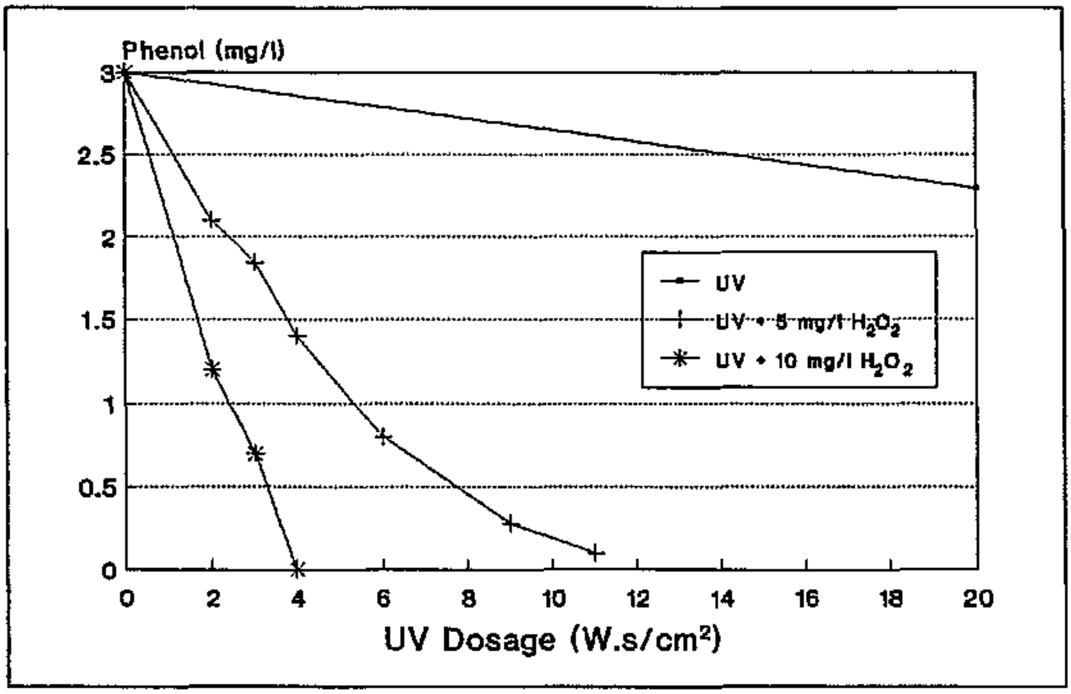


Figure 3.8 : Phenol removal by oxidation with ultraviolet irradiation (pH=7)

It is seen that oxidation with chlorine and ClO_2 are more effective under alkaline conditions. Oxidation with hydrogen peroxide as only oxidant was not successful.

Figure 3.8 shows phenol oxidation with ultraviolet irradiation as well as the combination of UV with H_2O_2. Little removal of phenol is taking place with UV alone, while the effectiveness of the process is greatly improved when H_2O_2 is added.

These experiments indicated that phenol :

- is slightly, (10%) more susceptible to oxidation with ozone than with PEROXONE. Where 52% removal of this compound was achieved with ozone, at neutral pH 47% removal of phenol was achieved witH PEROXONE;
- is not oxidised with H_2O_2;
- is successfully oxidised with chlorine and chlorine dioxide; and
- is not photolysed directly using UV radiation, but that the combination of UV and H_2O_2 can oxidise this compound.

3.2 Oxidation of DBS

DBS is used in pickling baths and detergent manufacture as well as in electronic cleaning chemicals. It can impart both undesirable taste and foaming to water. This component can end up in source waters due to washing of clothes in streams as well as industrial wastewater leakage.

For this investigation the same procedure was followed as for the oxidation of phenol. In this instance the water was spiked with DBS to a concentration of around 1.5 mg/ℓ. This water was ozonated at different pH levels to determine the effect of pH on the oxidation of the organic compound. In this instance, no removal was experienced at the acidic value. The change in effectiveness of DBS oxidation while increasing the pH value suggests that this compound is oxidised following the indirect pathway with hydroxyl radicals (Figure 3.9). Figure 3.10 shows the effect of H_2O_2 to O_3 ratio and it is seen that better removal of the compound is experienced at a mass ratio of 0.4 - 0.5.

Figure 3.11 shows the oxidation of DBS with PEROXONE at a H_2O_2/O_3 ratio of 0.4. Comparing these two processes in Figure 3.12, it is seen that the difference in effectiveness at pH 7 is larger than at pH 10. Because oxidation with ozone at pH 10 is also an advanced oxidation process with the ability to produce OH radicals, the difference between the PEROXONE and ozone process at the alkaline conditions is not very significant.

Figure 3.13 shows the oxidation of DBS using the combination of O_3 and UV. Results obtained here are similar to those obtained with PEROXONE as oxidant.

From Figure 3.14 it can be seen that no oxidation with chlorine of this compound is taking place at the acidic pH value of 4 while the compound is undergoing oxidation under alkaline conditions. The effect of oxidation with chlorine dioxide at the two pH values shows better removal of DBS under more alkaline conditions (Figure 3.15). Whereas H_2O_2 has been unsuccessful in the oxidation of phenol it is seen in Figure 3.16 that DBS is oxidised at a pH of 10.

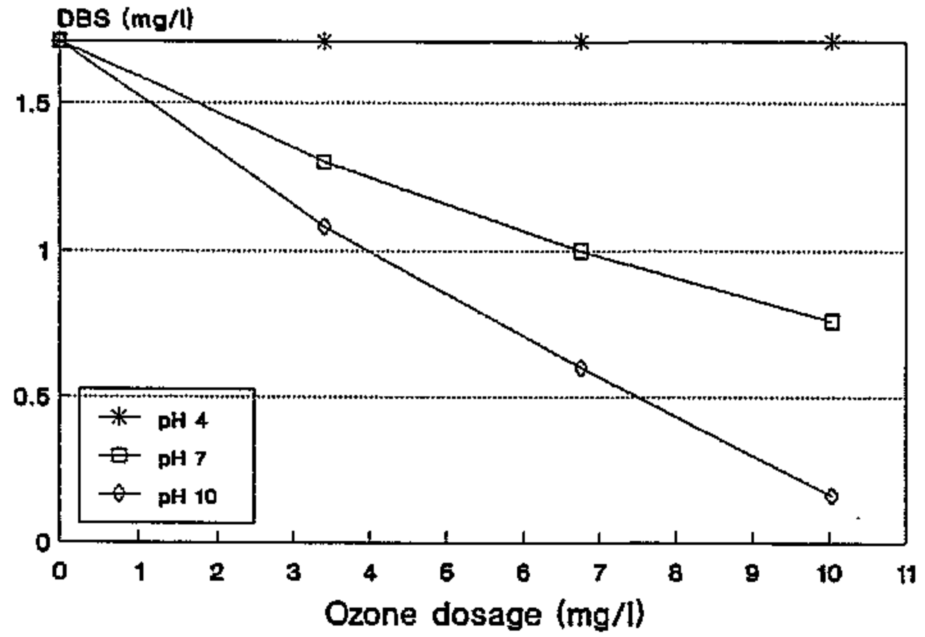


Figure 3.9 : DBS removal by oxidation with ozone

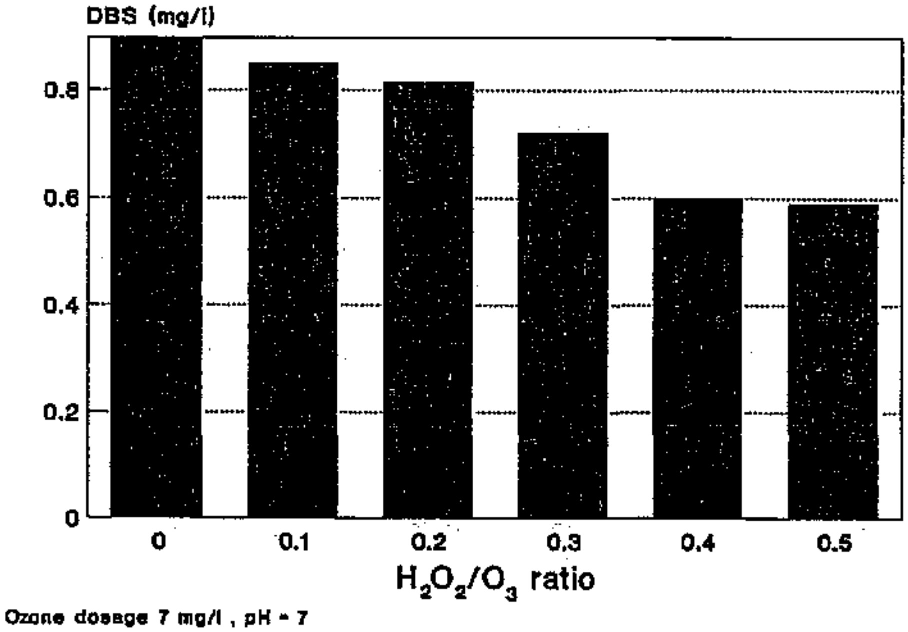


Figure 3.10 : Effect of H_2O_2/O_3 ratio on DBS removal by PEROXONE

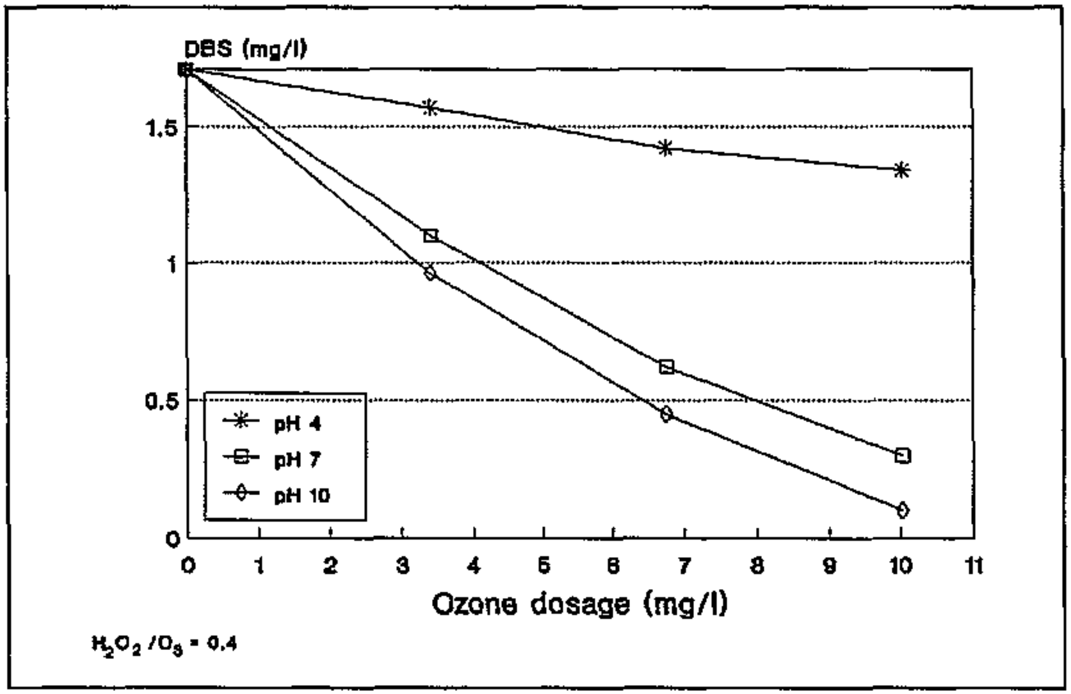


Figure 3.11 : DBS removal by oxidation with PEROXONE

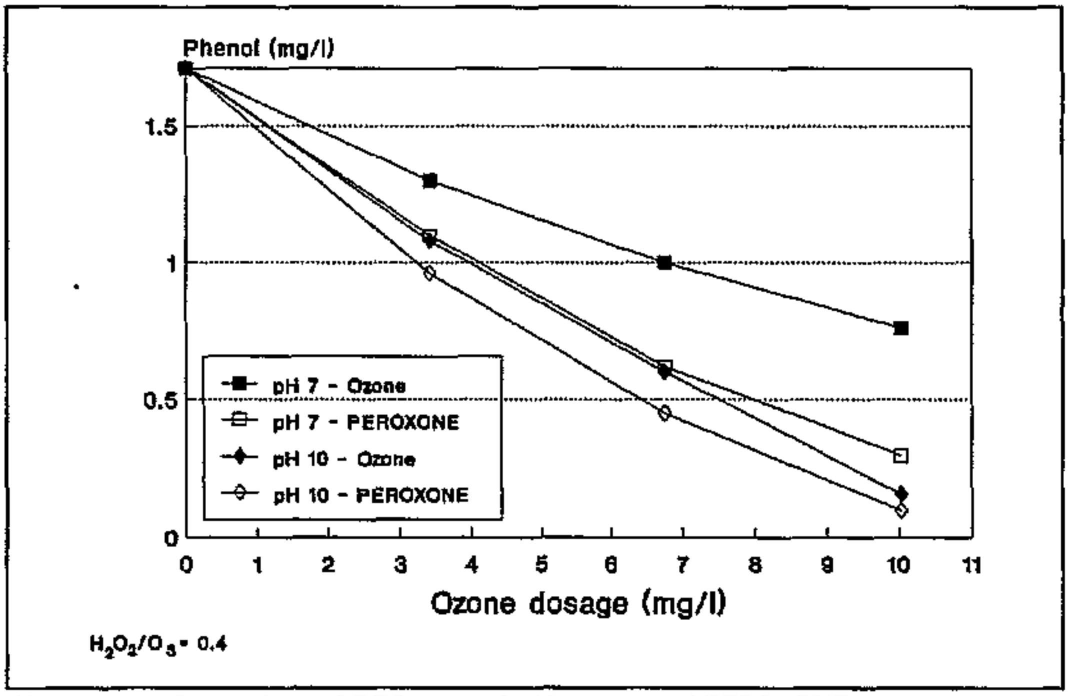


Figure 3.12 : Comparison of DBS removal with ozone and PEROXONE

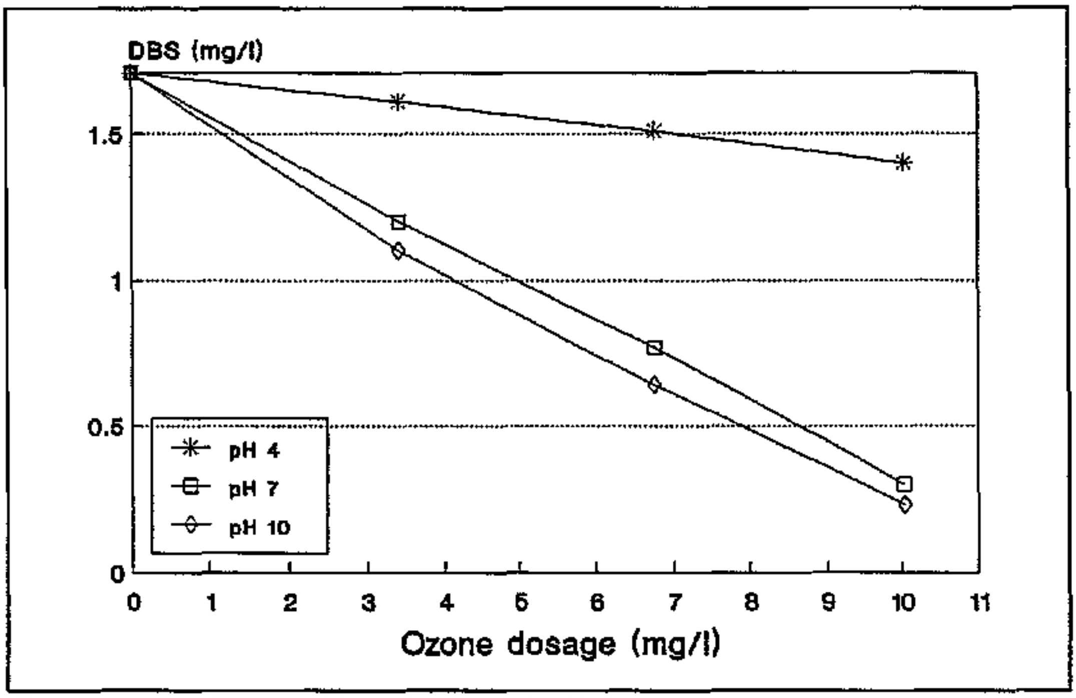


Figure 3.13 : DBS removal by oxidation with UV/O_3

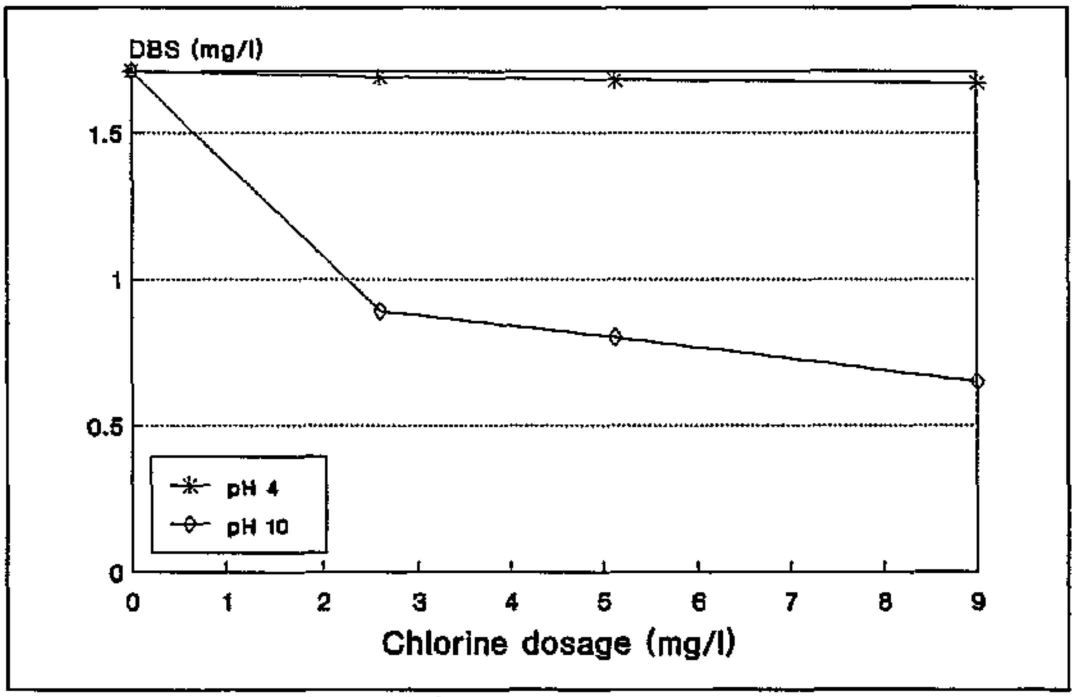


Figure 3.4 : DBS removal by oxidation with chlorine

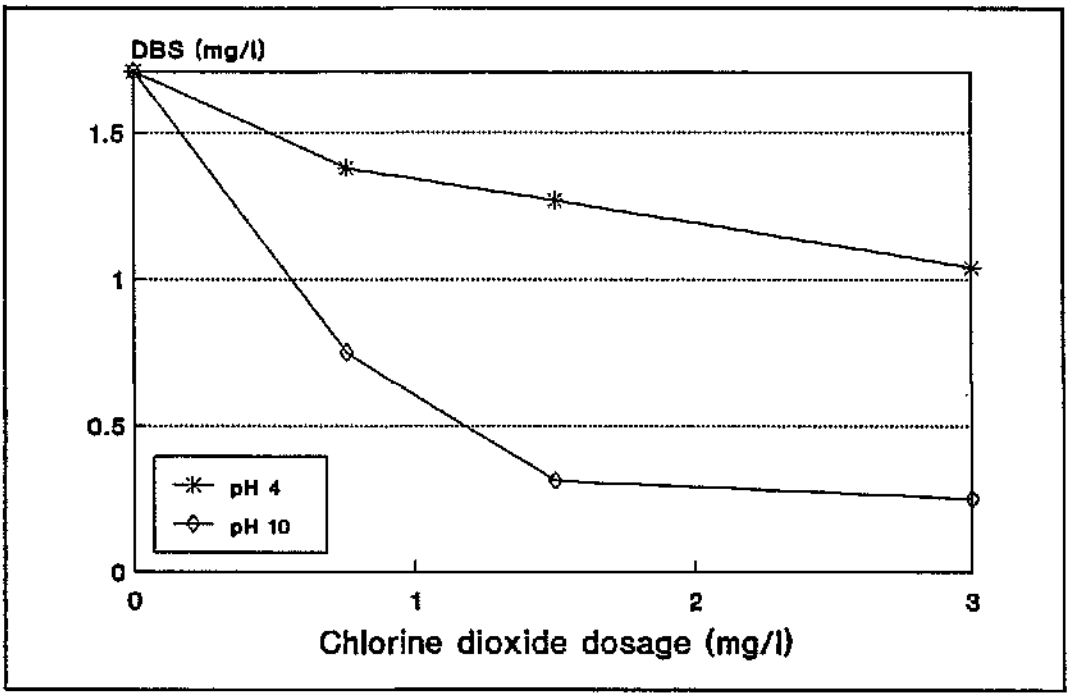


Figure 3.15 : DBS removal by oxidation with chlorine dioxide

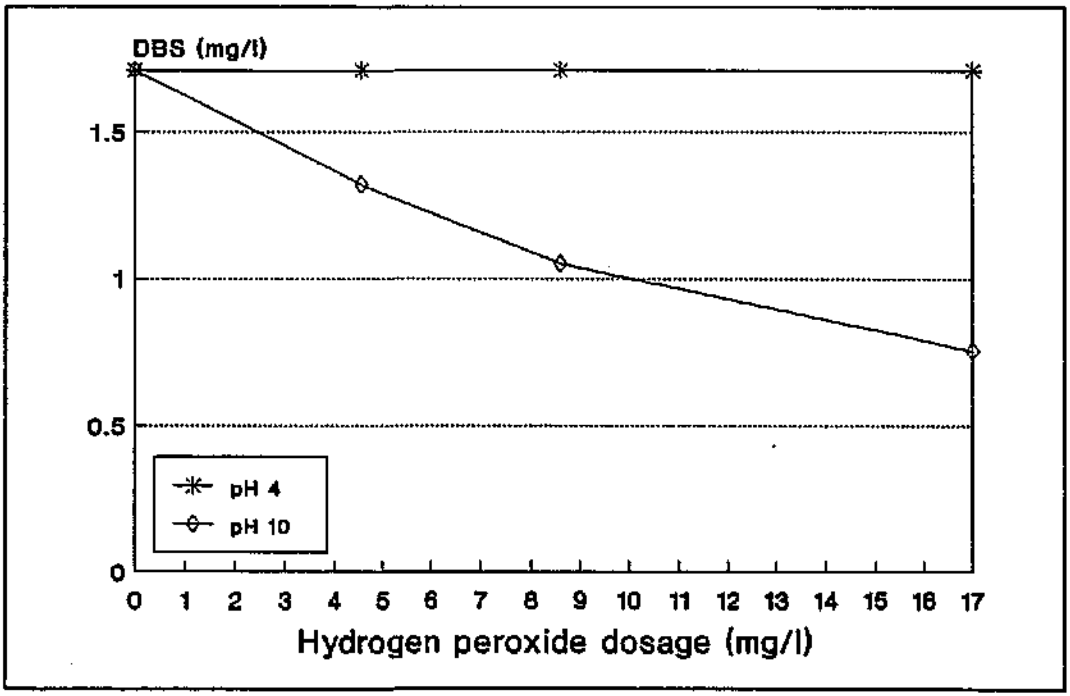


Figure 3.16 : DBS removal by oxidation with hydrogen peroxide

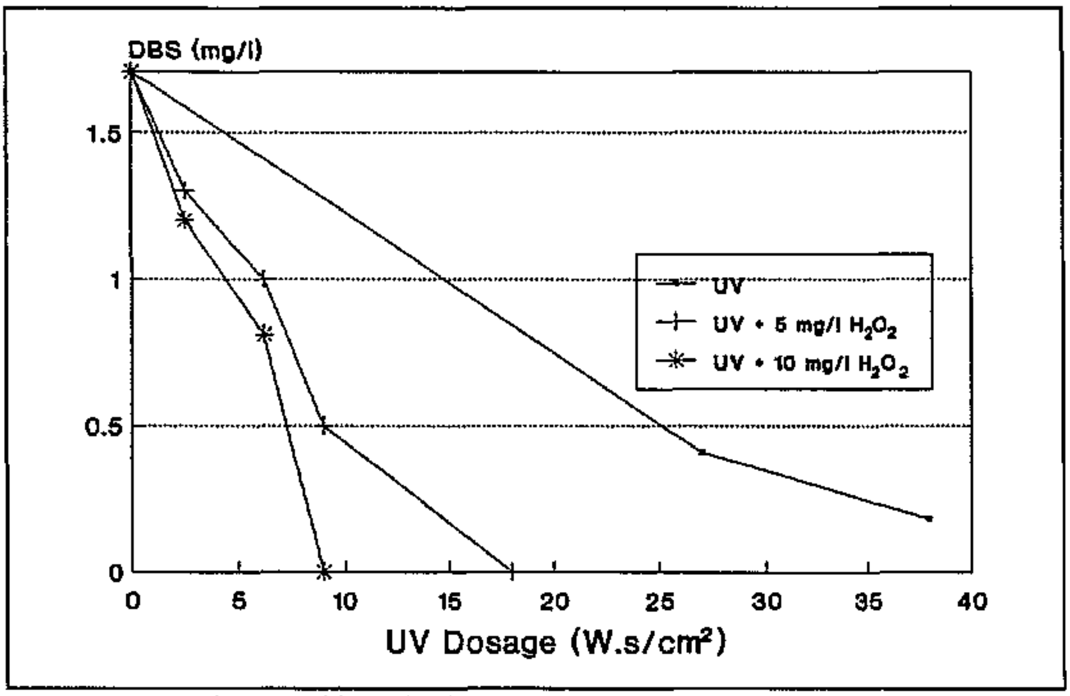


Figure 3.17 : DBS removal by oxidation with ultraviolet irradiation

Figure 3.17 shows the oxidation of DBS using the combination of ultraviolet irradiation and H_2O_2. The use of UV is on its own proved to be effective in oxidising this compound. The efficiency is also greatly improved with the addition of H_2O_2.

These experiments indicated that DBS :

- is more susceptible (50%) to oxidation with PEROXONE than with ozone. Where 82% removal of this compound was achieved with PEROXONE at a neutral pH, only 55% removal was achieved using ozone as oxidant.
- is oxidised with H_2O_2 under alkaline conditions;
- is oxidised with chlorine and chlorine dioxide; and
- is photolysed directly using UV radiation, and that the combination of UV and H_2O_2 enhances the efficiency of the process.

3.3 Removal of colour caused by humic acids

The colour of drinking water taken from lakes or rivers is often caused by humic substances. The stability of humic- and fulvic-acid molecules in water is largely due to a charge density imparted by acidic functional groups. Such colour causing compounds include numerous conjugated double bonds which are readily split by ozone oxidation, forming colourless saturated compounds.

The water used in this study was spiked by humic acid to produce, after filtering through a Watman filter no 1, a water with a true colour value of 50 mg Pt/ℓ. (True colour measures the colour of the water after all particulate matter has been removed). This value is equivalent to that found in surface waters in the South-Eastern Cape after treatment with conventional coagulation/filtration.

This water was ozonated at different pH levels to determine the effect of pH on colour removal. It can be seen from Figure 3.18 that colour removal under neutral and alkaline conditions are virtually the same, suggesting the fact that colour is removed following the direct ozonation reaction. Ozonation under acidic conditions was not successful, and in fact, the colour increased as ozonation continued. Figure 3.19 shows the effect of oxidation with PEROXONE and it is seen from Figure 3.20 that direct ozonation is much more effective for oxidation of colour caused by humic and fulvic acids. The use of O_3 + UV showed similar pattern as PEROXONE oxidation.

Colour was successfully removed using chlorine as an oxidant with removal of colour taking place under acidic and alkaline conditions (although at high dosages). The oxidation of colour using chlorine dioxide, however, was more effective under alkaline conditions. As with phenol removal, no removal of colour was found when H_2O_2 was used as an oxidant on its own. Figure 3.24 shows the effect of UV irradiation on colour removal and, it is seen that UV on its own doesn't have any effect on colour removal. The addition of H_2O_2 however, greatly improved the oxidation process.

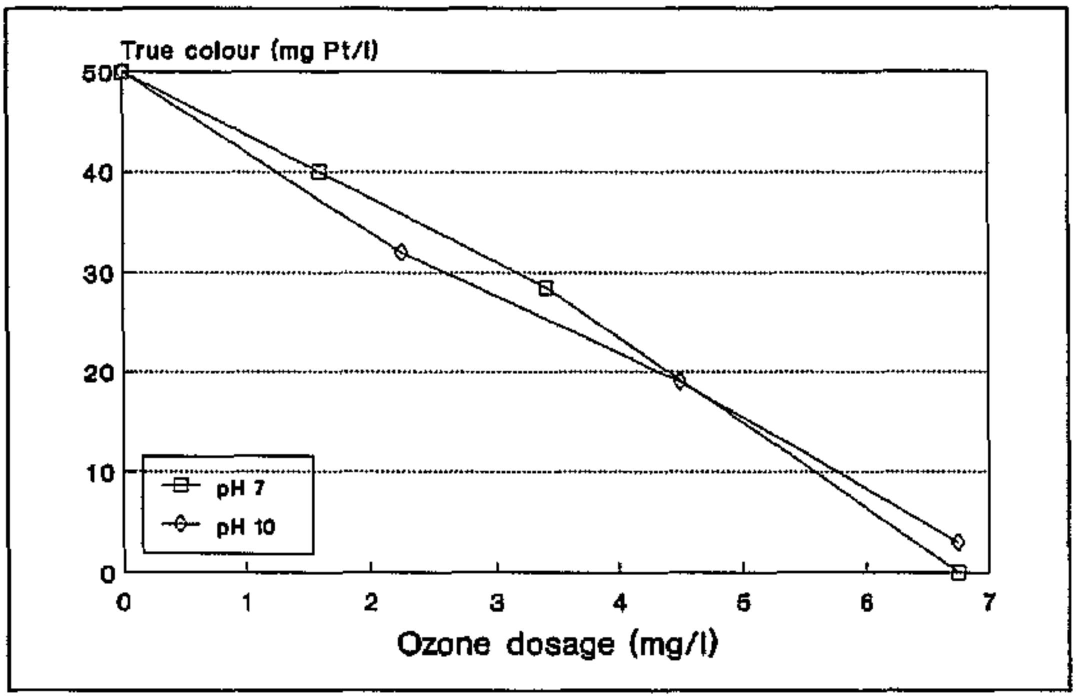


Figure 3.18 : Colour removal by oxidation with ozone

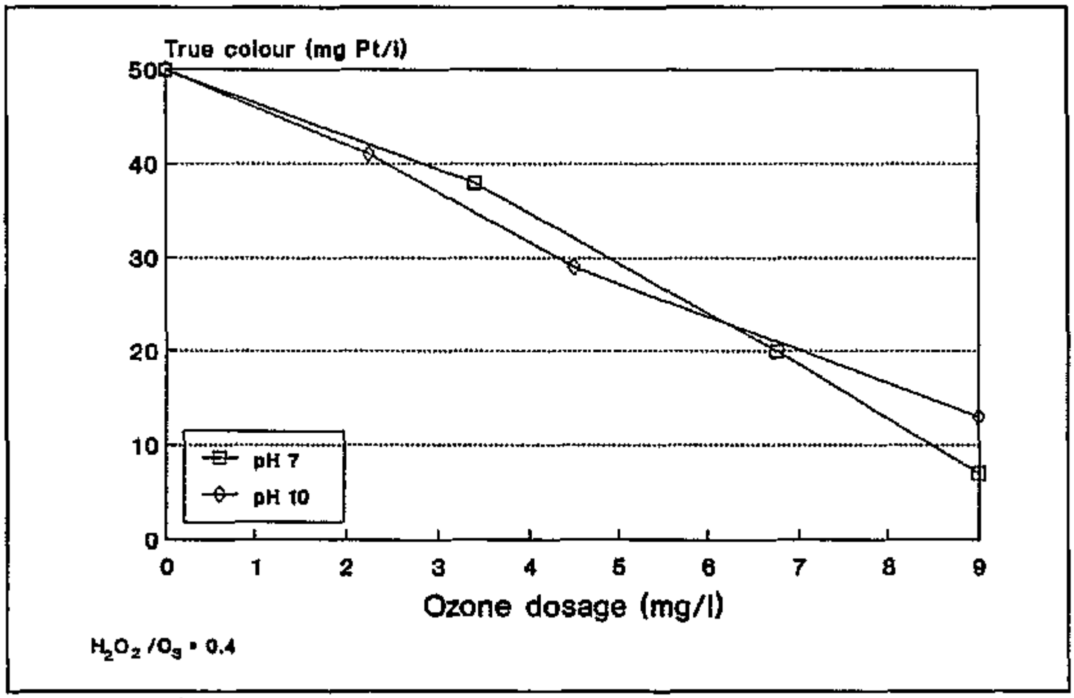
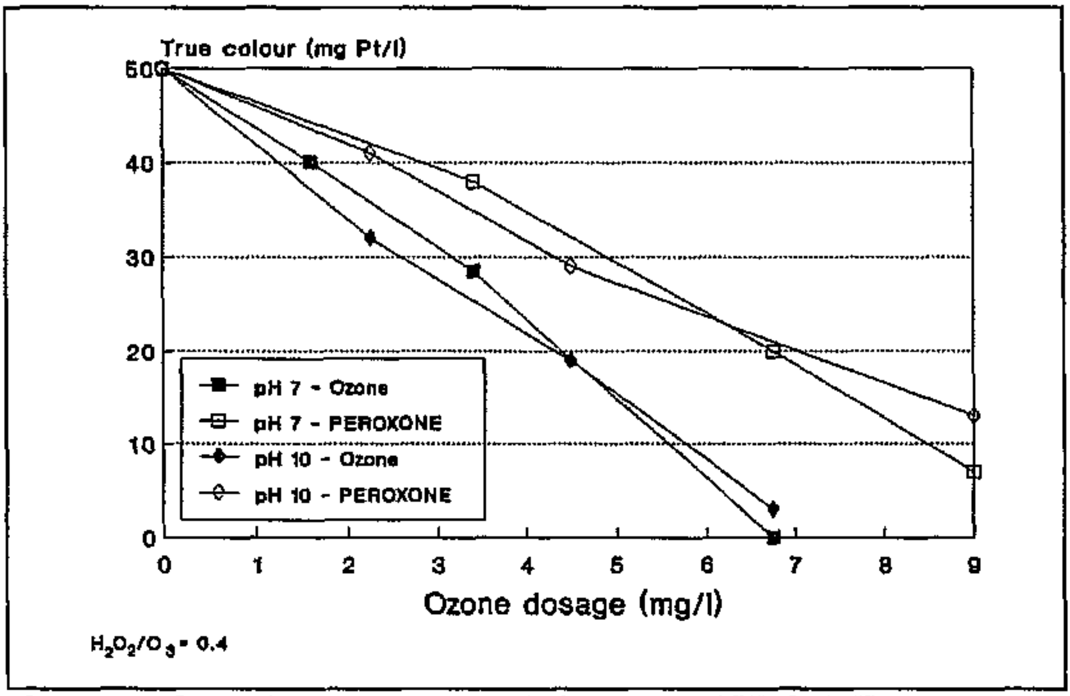


Figure 3.19 : Colour removal by oxidation with PEROXONE



$H_2O_2/O_3 = 0.4$

Figure 3.20 : Comparison of colour removal with ozone and PEROXONE

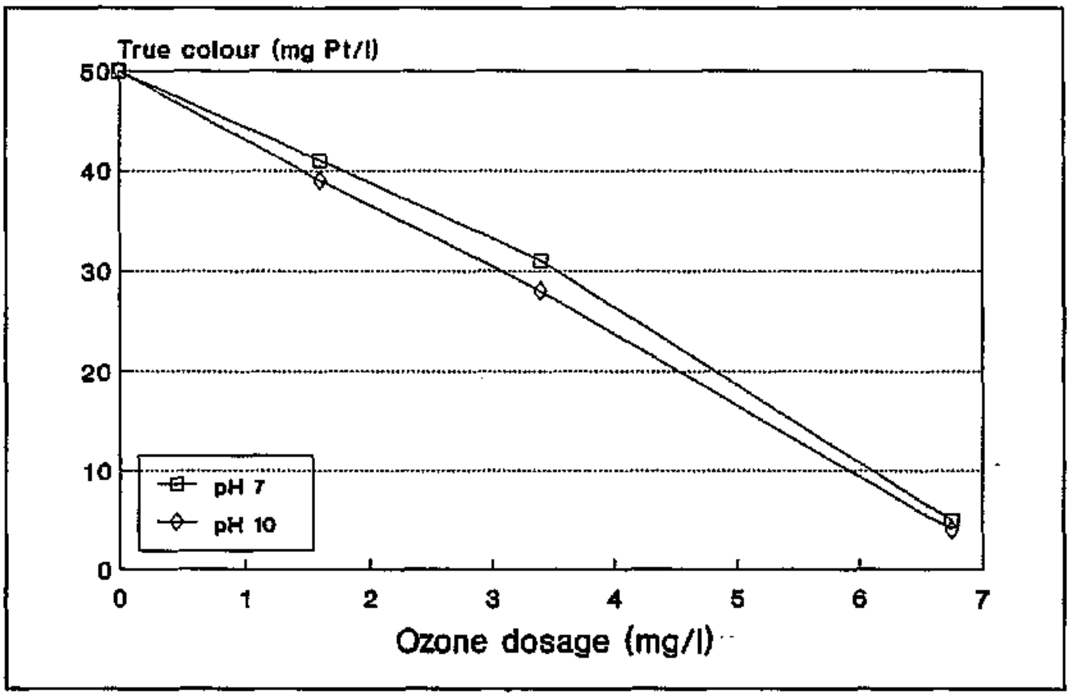


Figure 3.21 : Colour removal by oxidation with UV/O_3

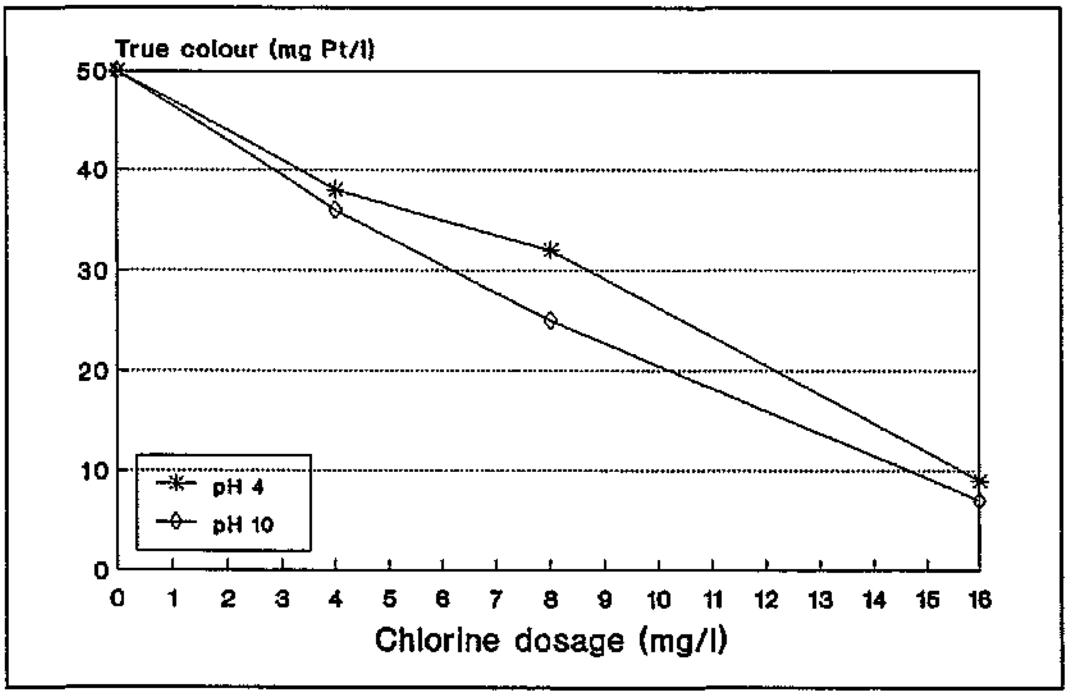


Figure 3.22 : Colour removal by oxidation with chlorine

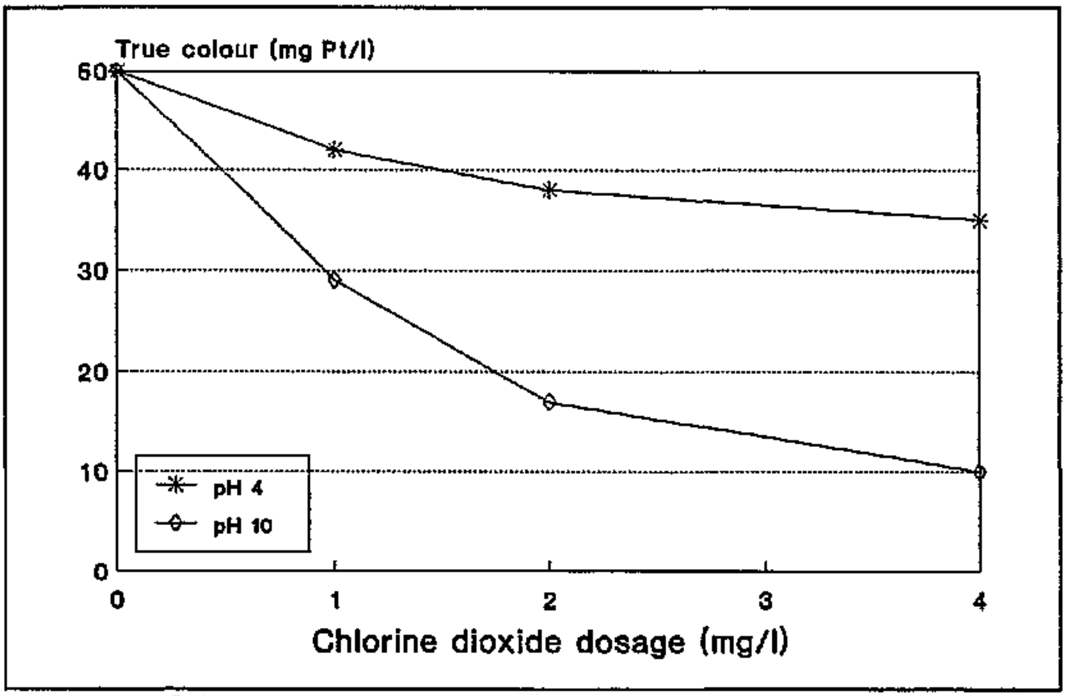


Figure 3.23 : Colour removal by oxidation with chlorine dioxide

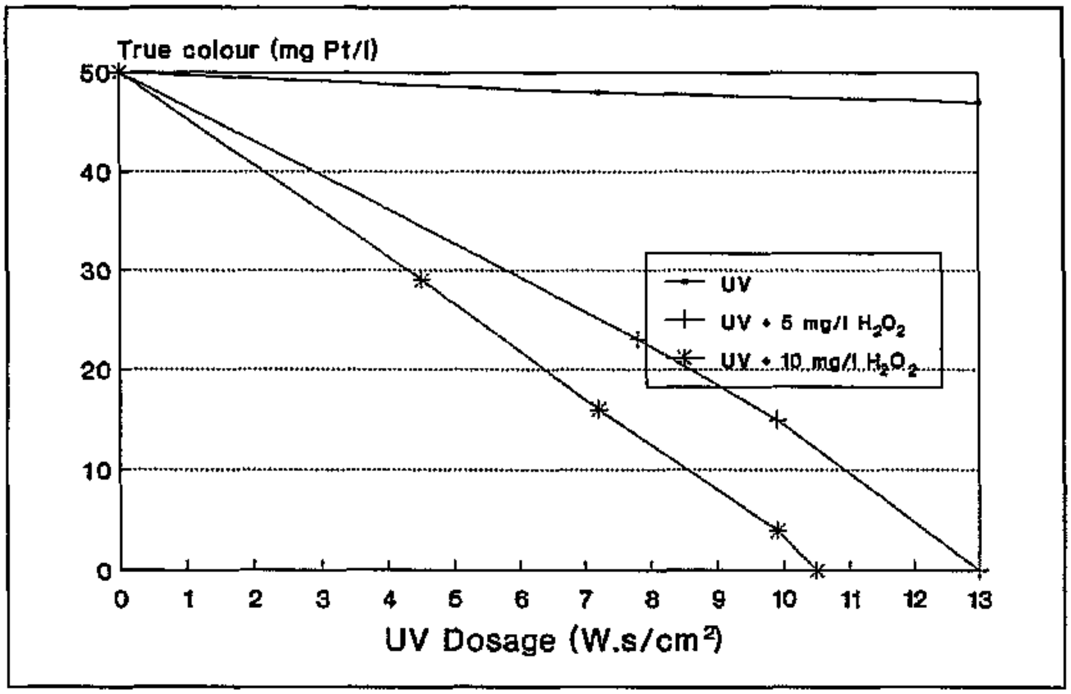


Figure 3.24 : Colour removal by oxidation with ultraviolet irradiation

These experiments indicated that colour :

- is more susceptible to oxidation with ozone than with PEROXONE. Under neutral conditions and at an ozone dosage of 6,8 mg/ℓ, 100% removal of colour was achieved using ozone, while only 50% removal of colour was obtained using PEROXONE;
- is not oxidised with H_2O_2;
- is oxidised with chlorine and chlorine dioxide; and
- is not photolysed directly using UV irradiation, but that the combination of UV and H_2O_2 can oxidise this compound.

3.4 Removal of taste and odours

In this experiment, water was spiked with 500 ng/ℓ of geosmin and MIB in separate containers. This water was treated at a neutral pH level with these oxidants under the following conditions:

- Ozonation continued until a change in colour in the KI solution occurred, showing that the ozone demand of the water was satisfied. This occurred at an ozone dosage of 21.4 mg/ℓ.
- H_2O_2 was added to the ozonation process and the same amount of ozone was added to the solutions containing the geosmin and MIB. In this case the KI solution changed colour after an ozone dosage of 15.8 mg/ℓ was added. Treatment, however was continued until 21.4 mg/ℓ was dosed.
- The solutions were also ozonated under UV light. An amount of 21.4 mg/ℓ of ozone

was added. A change in colour in the KI solution occured after 15.2 mg/ℓ of ozone was added.

- A UV dosage of 72 W.s/cm^2 was applied to the solutions. This was followed up by adding 20 mg/ℓ of H_2O_2 to the solution while undergoing UV irradiation.
- A chlorine dosage of 30 mg/ℓ was added to the solutions.
- A $C\ell O_2$ dosage of 10 mg/ℓ was added to the solutions.
- A H_2O_2 dosage of 20 mg/ℓ was added to the solutions.

The results of these experiments are shown in Table 3.1.

Table 3.1 : Oxidation of geosmin and MIB

Oxidant	Dosage	Residue (ng/ℓ)	
		Geosmin	MIB
Ozone	21.4 mg/ℓ	50	50
PEROXONE	21.4 mg/ℓ O_3 8.6 mg/ℓ H_2O_2	5	5
O_3/UV	21.4 mg/ℓ O_3 1.8 W.s/cm^2	5	5
UV	72 W.s/cm^2	200	200
UV/H_2O_2	72 W.s/cm^2 20 mg/ℓ H_2O_2	5	5
H_2O_2	20 mg/ℓ H_2O_2	500	500
$C\ell$	30 mg/ℓ	450	450
$C\ell O_2$	10 mg/ℓ	460	460

These experiments indicated that geosmin and MIB :

- is more susceptible to oxidation with PEROXONE than with ozone. Where 99% removal was obtained with PEROXONE, 90% removal was achieved using ozone as oxidant. This difference may seem small but this removal probably occured at 74% of the real dosage. Therefore, while being 10% more effective in removing these compound, this also may occur using 30% less ozone;
- is not oxidised succesfully with H_2O_2, chlorine or chlorine dioxide;
- is photolysed directly using UV radiation, and that the combination of UV and H_2O_2 enhances the effectiveness of the process.

3.5 Oxidation of eutrophic water from Western Transvaal Regional Water Company

The aim of this experiment was to investigate the effect of the addition of different oxidants, to the water of the Western Transvaal Regional Water Company, on the formation of trihalomethane compounds and organic content in the water. The pH was 7.82 and the alkalinity 86 mg/ℓ. Table 3.2 shows the results of this study.

Table 3.2 : Effect of different oxidants on the organic content in water from the Western Transvaal Regional Water Company

Oxidant and conditions	Trihalomethane formation potential (µg/ℓ)				Total trihalomethane formation potential (µg/ℓ)	Dissolved organic carbon (mg/ℓ)	Total organic carbon (mg/ℓ)
	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$			
Raw Water	28	44	33	56	161	9.9	25
Ozone (1.5 mg/ℓ)	36	46	23	22	127	10.5	29
Ozone (3 mg/ℓ)	41	47	24	24	136	10.3	29
PEROXONE (1.5 mg/ℓ + 0.6 mg/ℓ H_2O_2)	44	50	24	22	140	10.4	28
PEROXONE (3 mg/ℓ + 1.3 mg/ℓ H_2O_2)	39	47	24	23	133	10.5	27
UV (100 W.s/cm^2)	39	47	23	19	128	11.7	27
UV (100 W.s/cm^2 + 5 mg/ℓ H_2O_2)	35	44	21	20	120	9.5	26
Peroxide (2 mg/ℓ)	41	47	23	22	133	10.7	27
Peroxide (8 mg/ℓ)	40	49	23	21	133	9.9	26
Chlorine (2 mg/ℓ)	35	44	23	28	130	10.2	25
Chlorine (8 mg/ℓ)	43	46	25	29	143	10.8	26
Chlorine dioxide (1 mg/ℓ)	37	44	24	30	135	11.4	27
Chlorine dioxide (5 mg/ℓ)	43	48	25	25	141	10.9	26

Generally, it was found that :

- the DOC and TOC content of the water increased. This is probably due to the oxidation of algae in the water to the extent that organic material is made more soluble in the water;

- an increase in ozone dosage led to the formation of more trihalomethanes. This is due to the fact that some organics in the water are oxidised and become more susceptible to formations with halogen compounds. The addition of H_2O_2 to ozone led either to the amount of organics in the water being more oxidised (decrease in TOC and DOC) with an increase in THM formation, or the conditions staying virtually the same. The latter might be due to scavenging of the OH radicals by bi-carbonates and carbonates in the water;
- the increase in chlorine and chlorine dioxide dosages led to higher THM values; and
- an increase in hydrogen peroxide dosage had no effect on further THM formation.

3.6 Oxidation of eutrophic water from Umgeni Water

Water for this study was obtained from the Wiggans Waterworks in Durban. This plant receives its water from an impounded source which is known for its eutrophic conditions. Water obtained for the study had a pH of 8,1 with an alkalinity of 55 mg/ℓ. The aim of the experiment was to evaluate the effect of the addition of different oxidants on the formation of trihalomethanes. Table 3.3 shows the results of this experiment.

Table 3.3 : Effect of different oxidants on trihalomethane formation - Umgeni Water

Oxidant and conditions	Trihalomethanes - µg/ℓ formed (potential in brackets)				Total trihalomethanes (µg/ℓ) formed (potential)
	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	
Raw Water	0 (25)	0 (35)	0 (14)	0 (4)	0 (78)
Ozone (1 mg/ℓ)	0 (21)	0 (38)	0 (17)	0 (0)	0 (76)
Ozone (2 mg/ℓ)	0 (23)	0 (36)	0 (16)	0 (3)	0 (78)
PEROXONE (1 mg/ℓ)	0 (20)	0 (35)	0 (16)	0 (3)	0 (74)
PEROXONE (2 mg/ℓ)	0 (23)	0 (35)	0 (17)	0 (0)	0 (75)
UV (9 Ws/cm^2)	0 (29)	0 (36)	0 (17)	0 (7)	0 (89)
UV (18 Ws/cm^2)	0 (33)	0 (37)	0 (17)	0 (3)	0 (90)
UV + H_2O_2 (9 WS/cm^2 +2 mg/ℓ)	0 (31)	1 (34)	0 (17)	0 (6)	1 (88)
UV + H_2O_2 (18 WS/cm^2 +2 mg/ℓ)	0 (32)	0 (33)	0 (20)	0 (7)	0 (92)
Chlorine (2 mg/ℓ)	4 (23)	17 (36)	9 (17)	0 (8)	30 (84)
Chlorine (4 mg/ℓ)	7 (23)	19 (33)	10 (15)	0 (0)	36 (71)
Chlorine dioxide (1 mg/ℓ)	1 (17)	2 (32)	0 (17)	0 (17)	3 (83)
Chlorine dioxide (2 mg/ℓ)	0 (12)	2 (27)	0 (14)	0 (5)	2 (58)

Generally it was found that:

- the addition of ozone and PEROXONE to this water at the applied dosages had no effect on the THM formation potential;
- UV irradiation led to higher THM formation potential values while the addition of H_2O_2 under UV irradiation had no effect on THM potential value. This suggests that the formation of OH radicals do not have an effect on oxidation, as is also witnessed in the PEROXONE results. This effect is probably due to scavenging of the OH radicals by bicarbonates and carbonates in the water;
- an increase in chlorine dosing led to the formation of more trihalomethanes although a decrease in formation potential is witnessed;
- an increase in chlorine dioxide dosing led to a lower potential of THM formation indicating that either the properties of the organics are changed to depress THM formation or that effective oxidation occurs resulting in less organics available for THM formation.

3.7 Oxidation of Cape Brown Water

Water for this study was obtained from the Kleinbrak waterworks which is situated some 15 kilometres from Mosselbaai. This water is characterised by very low alkalinity of 5 mg/ℓ and a pH of between 2.5 and 3.5. Treatment at this works consist of pH adjustment with lime followed by flocculation, sedimentation and filtration. The pH of the water was adjusted to 7, buffered and diluted with deionised water until a water with a true colour of 50 mg Pt/ℓ was obtained. In order to investigate the effect of alkalinity on especially the advanced oxidation processes, $NaHCO_3$ was added to the water to produce higher values of alkalinity.

Similar tests as described in section 3.3 were conducted on this water while the formation of trihalomethanes were also investigated under certain oxidation conditions. These conditions were chosen so as to produce a final water with a true colour value of around 20 mg Pt/ℓ (except in the case of $C1O_2$).

Table 3.4 shows the results of this experiment.

Table 3.4 : Effect of different oxidants on organic content - Cape Brown Water

Oxidant and conditions	Colour after oxidation (mg pt/ℓ)	Dissolved organic carbon (DOC, mg/ℓ)	Triholemethanes (mg/ℓ) formed (potential)
Raw water	-	5,1	0 (159)
Ozone (6 mg/ℓ)	18	4,1	6 (167)
PEROXONE (8 mg/ℓ)	18	4,6	2 (152)
UV + H_2O_2 (10 WS/cm^2 + 10 mg/ℓ)	20	4,2	1 (91)
Chlorine (16 mg/ℓ)	25	5,4	142 (165)
Chlorine dioxide (4 mg/ℓ)	45	4,9	8 (175)

From Table 3.4 it can be seen that:

- a lower THM formation potential is realised when PEROXONE is dosed as compared with ozone treatment and that fewer THM's are actually formed with PEROXONE. At the same time the DOC content with ozone treatment is reduced moreso than with PEROXONE treatment. This suggests that oxidation by ozone produces end products which are more susceptible to THM formation than when PEROXONE is used as oxidant. This is also due to more effective oxidation with ozone than with PEROXONE;
- the advanced oxidation process of UV and H_2O_2 leads to a lower THM formation potential value while also leading to a lower DOC value in the water. The byproducts and/or end products of oxidation using this oxidant are therefore less susceptible to THM formation if compared to ozone treatment where the final DOC in the water are about the same for the two processes;
- the addition of chlorine dioxide to the water leads to less THM's formed if compared to the chlorine process.

Oxidation with chlorine and chlorine dioxide were both more effective at the higher alkalinity of 71 mg/ℓ than at an alkalinity of 5 mg/ℓ (Figures 3.25 and 3.26). Comparing Figures 3.27 and 3.28 it can be seen that UV oxidation as well as the advanced oxidation process of UV/H_2O_2 are more effective at the lower alkalinity value. It is therefore clear to see that an increase in alkalinity inhibits the oxidation process (in this case the action of the OH radicals). The inhibiting effect of carbonate ions is also seen from Figure 3.29 where oxidation with ozone and PEROXONE at different alkalinity values were performed. As the alkalinity increases, the effectiveness of the oxidation process decreases.

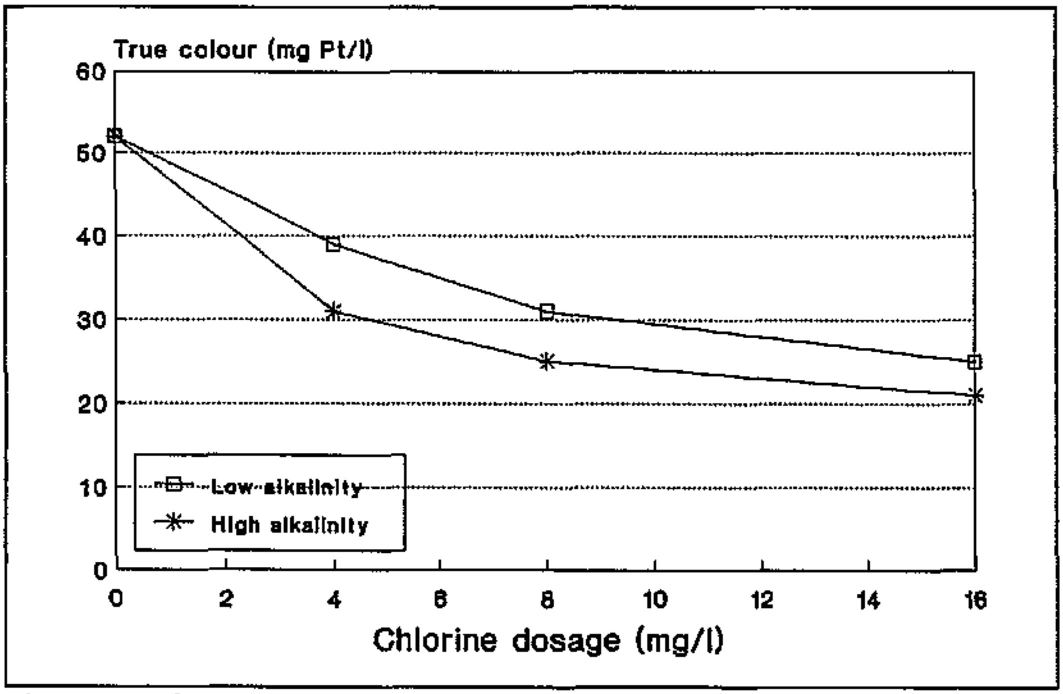


Figure 3.25 : Colour removal by oxidation with chlorine (Cape Brown Water)

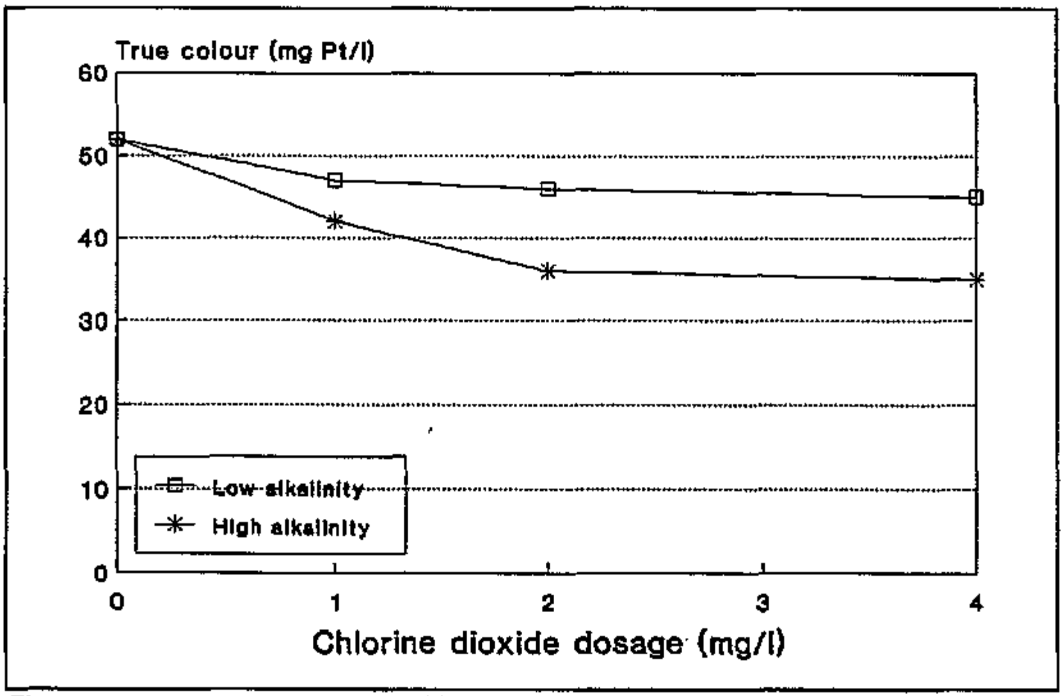


Figure 3.26 : Colour removal by oxidation with chlorine dioxide (Cape Brown Water)

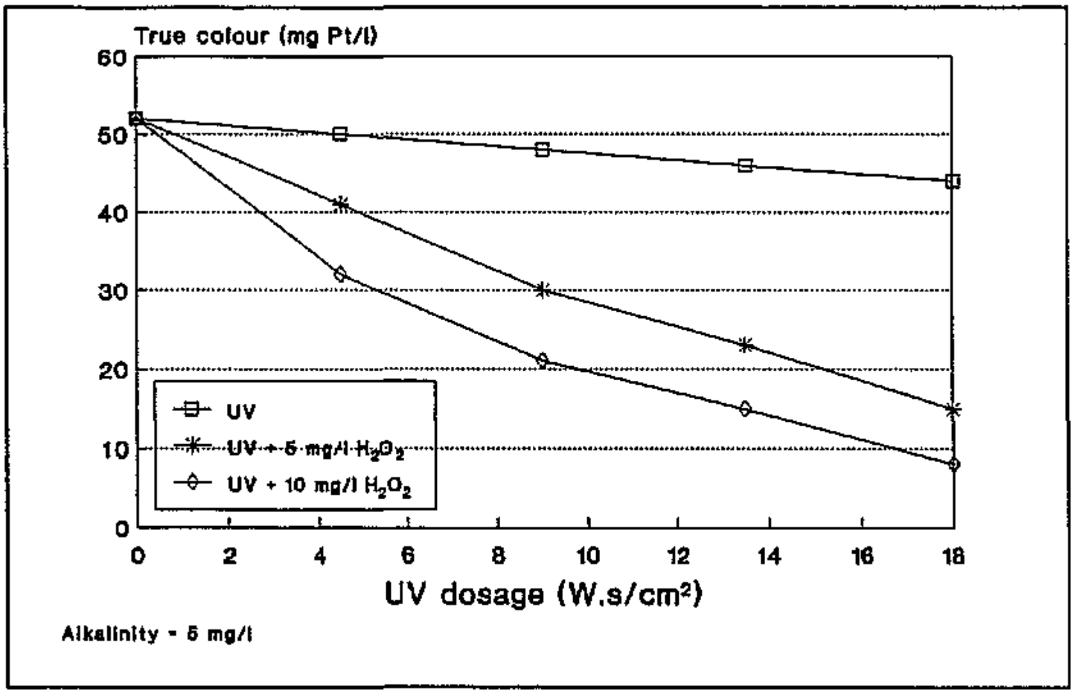


Figure 3.27 : Colour removal by oxidation with UV and UV/H_2O_2 - low alkalinity

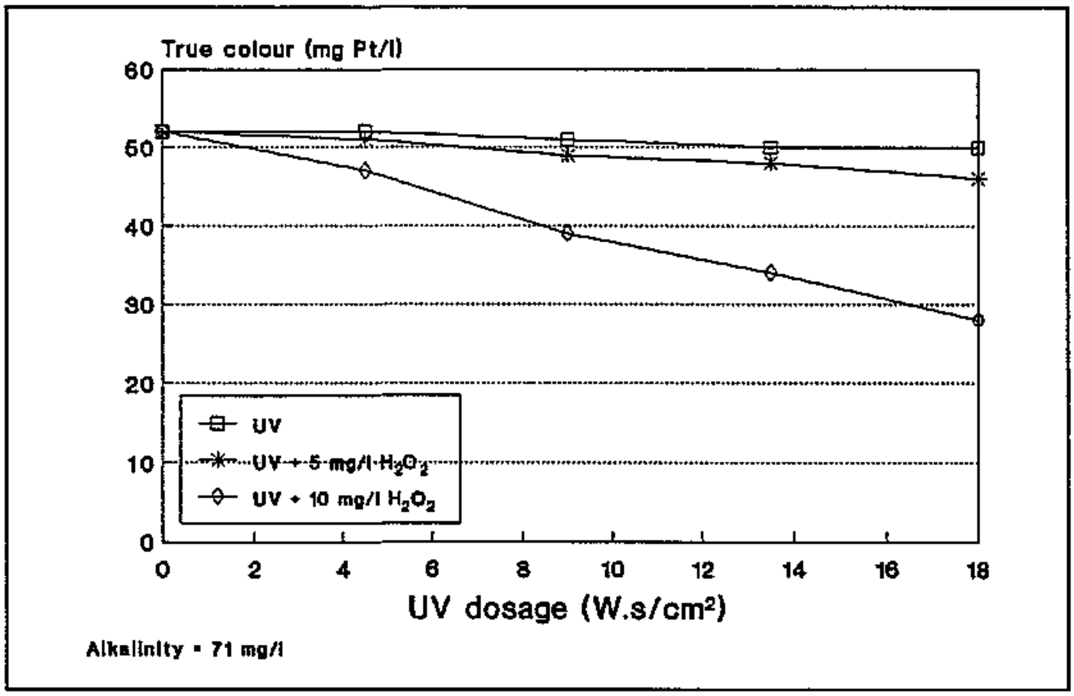


Figure 3.28 : Colour removal by oxidation with UV and UV/H_2O_2 - high alkalinity

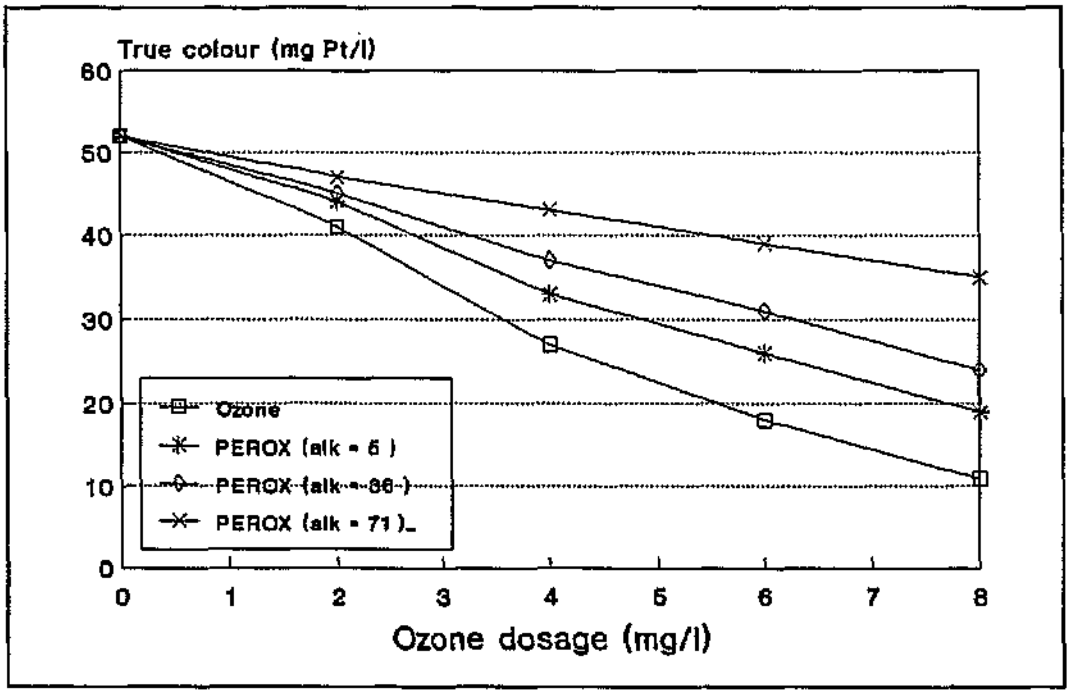


Figure 3.29 : Colour removal by oxidation with ozone and PEROXONE (Cape Brown Water)

3.8 Effect on Coagulation/Flocculation

The objective of this experiment was to determine whether the addition of ozone to raw water had any influence on the flocculation requirements of the water. Water for this study was obtained from the Wilge river. This water had a pH of 7,87 and a turbidity of 28 NTU at the time of the study. The coagulant used for this study was a cationic polymer which required an optimum dose of 6 mg/ℓ with this water.

The water was ozonated whereafter the coagulant was added to the water. This water was stirred at 100 rpm for four minutes whereafter the speed was reduced to 40 rpm for a further 10 minutes. After the stirrers were stopped, turbidity tests were carried out on the water and evaluated according to the test of aggregation (Polasek, 1980). This test was repeated for different ozone dosages and different coagulant dosages.

3.8.1 Test of Aggregation

The test of aggregation gives an indication of the proportional presence of partial size fractions of particles in a system. Thus the test of aggregation facilitates the evaluation of particle size distribution, expressed by the distribution of settling velocities. It further offers the possibility of determining the character of particles being formed. The test of aggregation is suitable for

3.8.2 Results

The results of these tests are tabulated in Table 3.5 and shown graphically in Figure 3.30 to 3.36.

Table 3.5 : Effect of ozone on Coagulation/Flocculation

O_3 Dosage	Turbidity(NTU)											
	2 mg/ℓ SUPERFLOC				4 mg/ℓ SUPERFLOC				6 mg/ℓ SUPERFLOC			
	Macro	Micro	Fugate	pH end	Macro	Micro	Fugate	pH end	Macro	Micro	Fugate	pH end
0	6,1	4	2,2	7,85	3,6	2,6	1,2	7,84	1,8	1,5	0,6	7,84
1	7,8	5,3	2,7	7,56	3,9	2	0,9	7,68	3,4	1,2	0,6	7,74
2	9,5	5,3	2,6	7,81	5,3	2,8	1,2	7,60	4,2	1,5	1,2	7,60
3,5	5,5	5	2,2	7,29	1,7	1,3	0,8	7,36	1,8	0,6	0,3	7,24

It can be seen that with an increase of ozone up to 2 mg/ℓ, the proportion of macro particles decreased while the proportion of micro particles increases. This indicates a detrimental effect of ozone on flocculation. It is however witnessed that with an increase of ozone to 3,5 mg/ℓ, this negative impact is reversed and a better quality water in terms of turbidity is obtained.

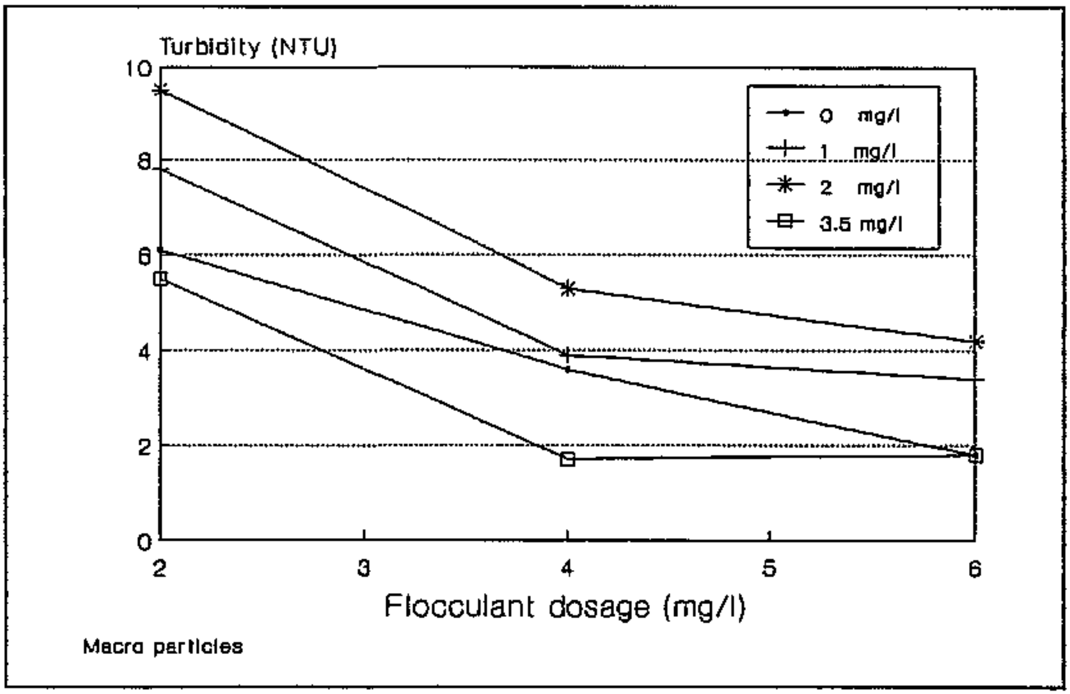


Figure 3.30 : Turbidity after removal of macro particles

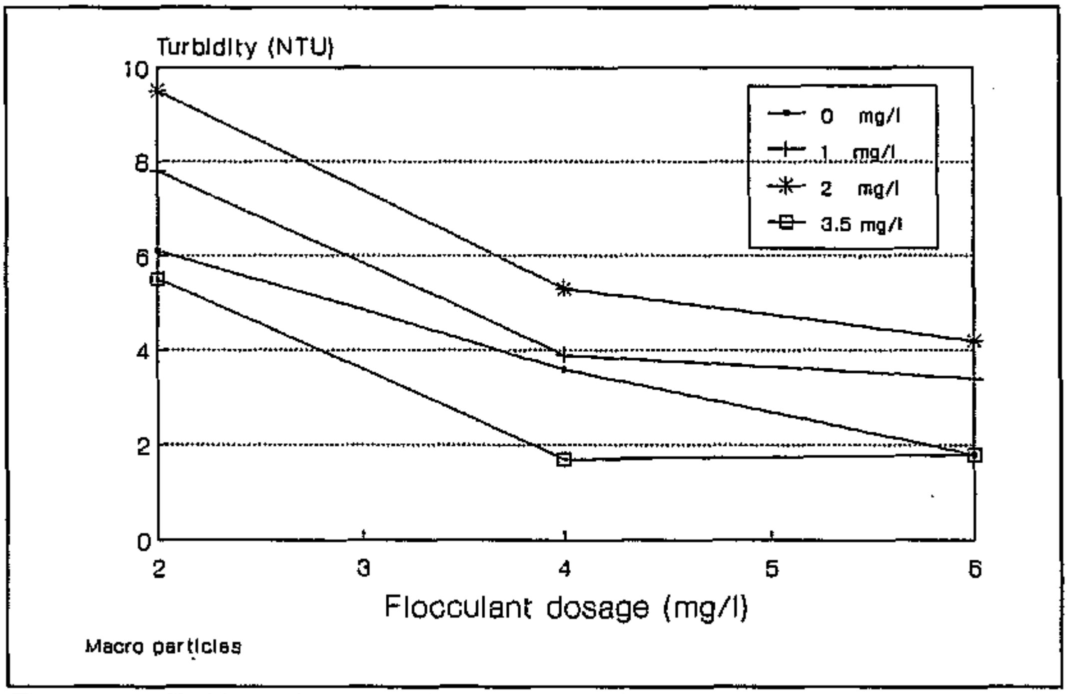


Figure 3.30 : Turbidity after removal of macro particles

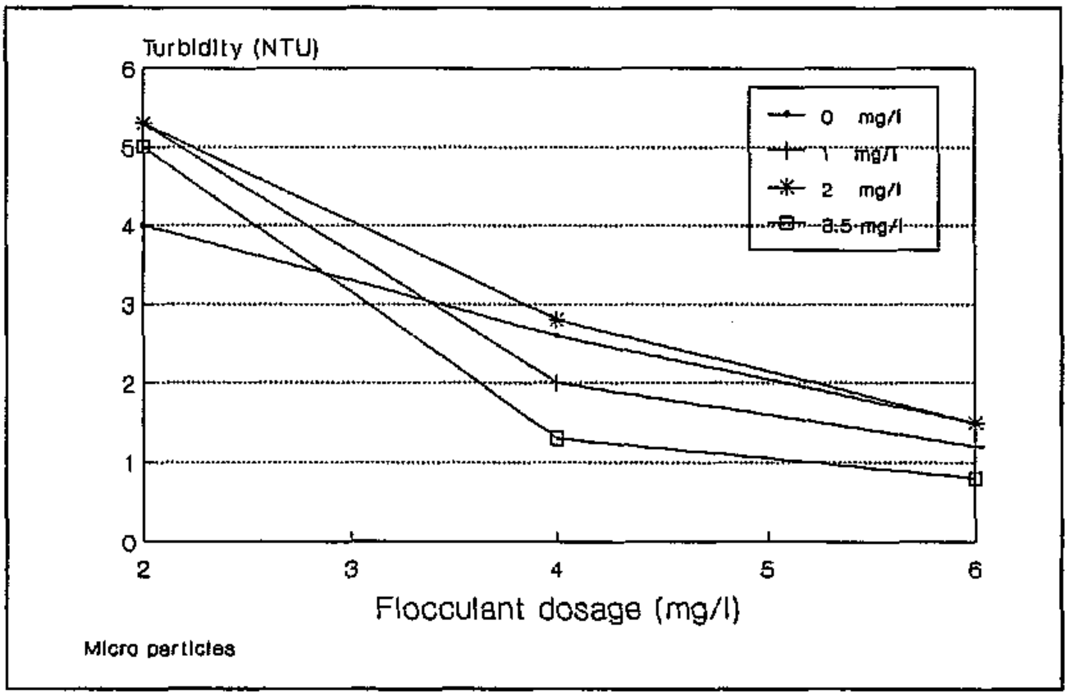


Figure 3.31 : Turbidity after removal of micro particles

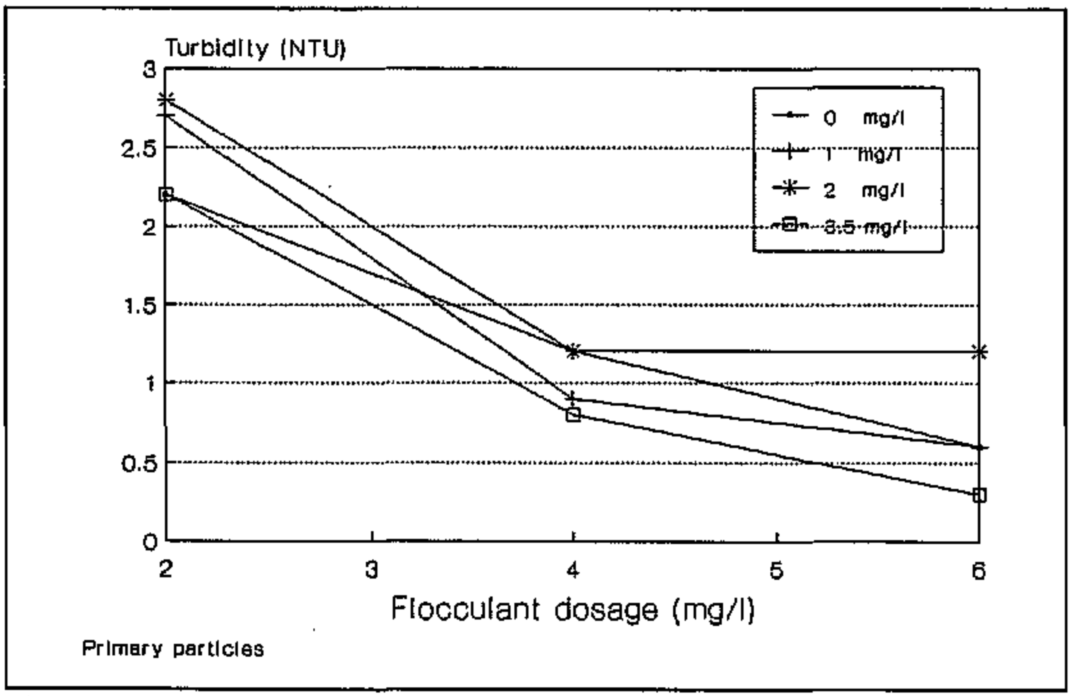


Figure 3.32 : Turbidity after removal of primary particles

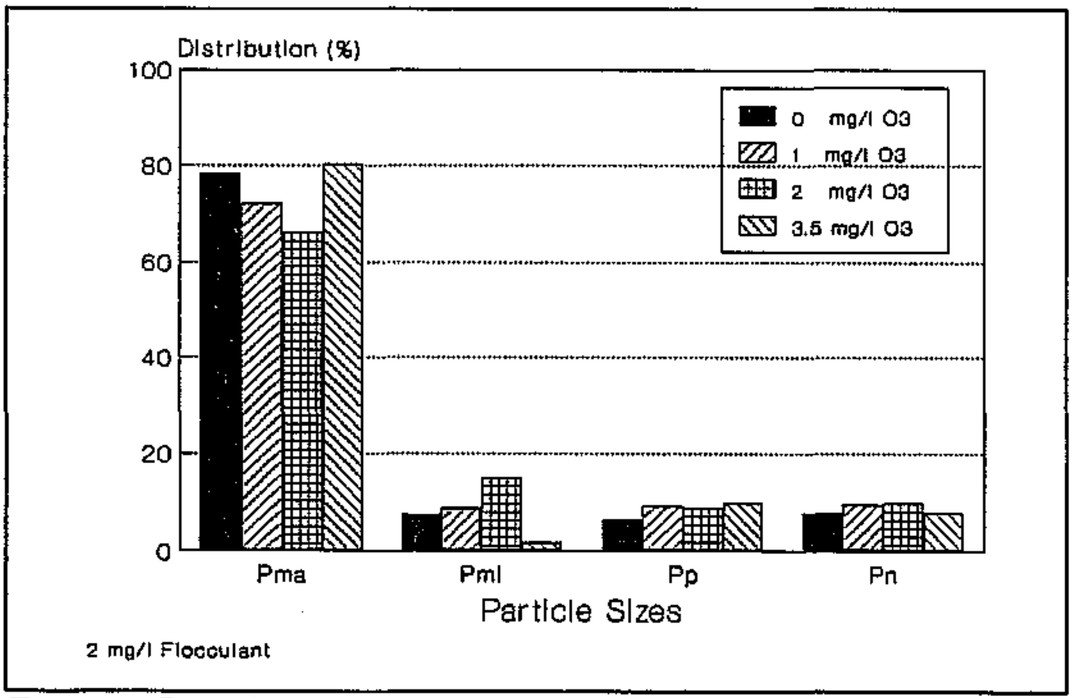


Figure 3.33 :Proportion of different particle sizes in treated water - 2 mg/ℓ Superfloc

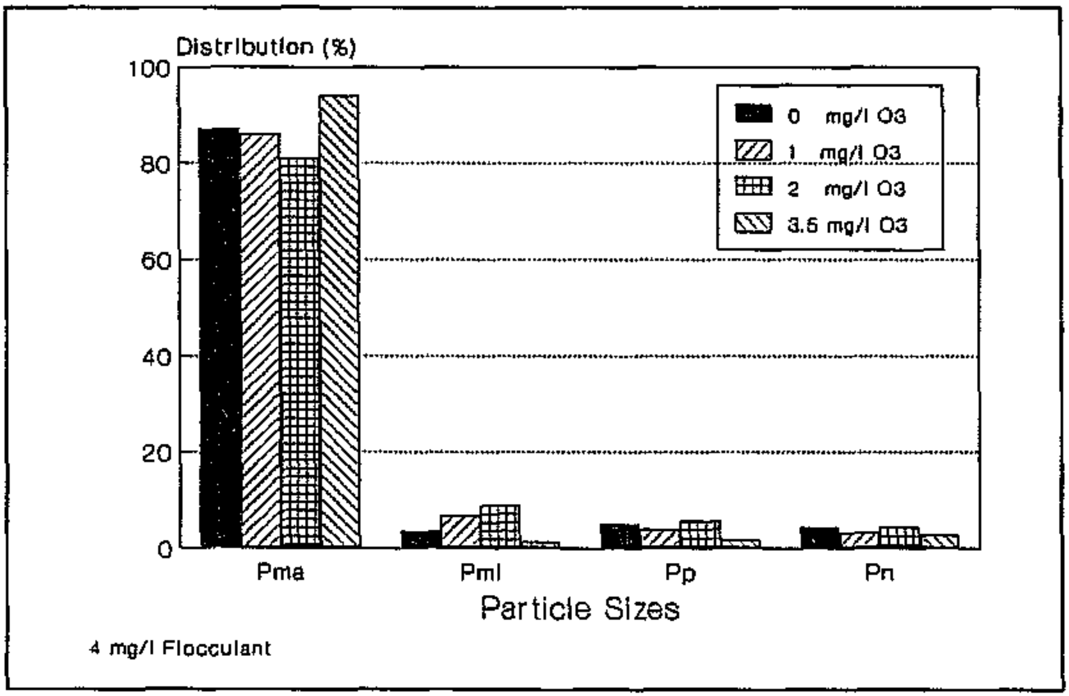


Figure 3.34 :Proportion of different particle sizes in treated water - 4 mg/ℓ Superfloc

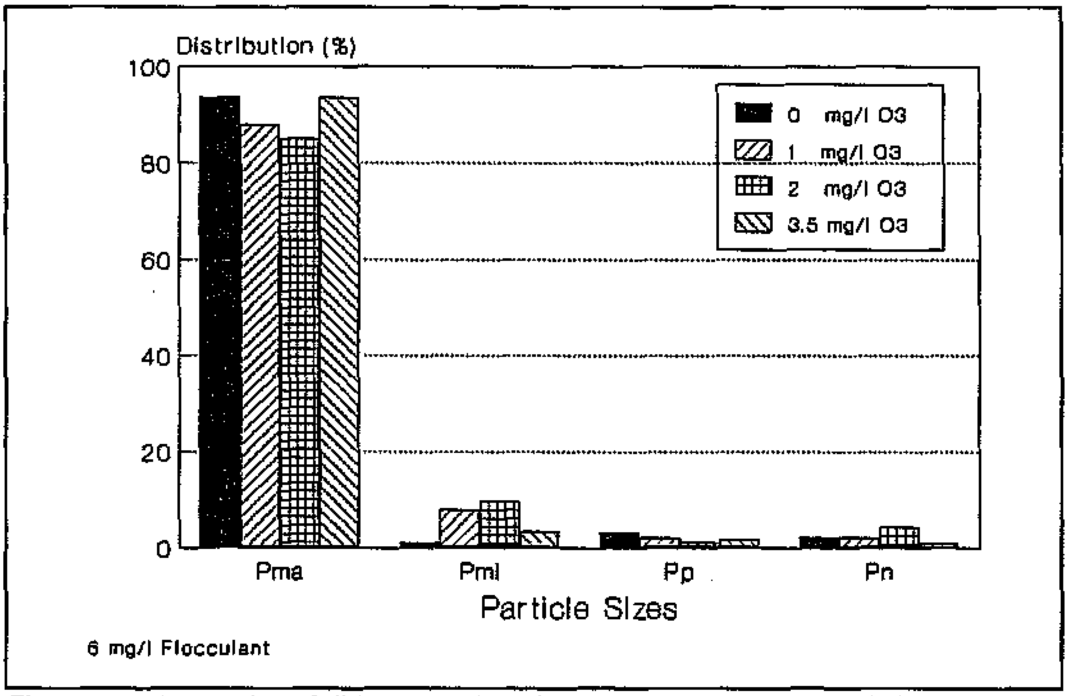


Figure 3.35 :Proportion of different particle sizes in treated water - 6 mg/ℓ Superfloc

CHAPTER 4 : PILOT PLANT STUDY

4.1 Cape brown water

This pilot plant study was conducted at the Kleinbrak Water Treatment Works situated about 15 kilometres northeast of Mosselbay. An OREC (Ozone Research and Equipment Corporation) ozonator was used which had a full load capacity of 4 g O_3/hr. The ozonator comprised of an air processing and ozone generator system. The ozone reactor was a 4m high uPVC column with a diameter of 50 mm. Raw feed water was introduced at the top of the column while ozonated air was introduced at the base of the column, hence resulting in counter current flow. Water samples were collected from the raw water and ozonated water sample points and analysed on site for true colour. At the time of the study the alkalinity of the water was 5 mg/ℓ as $CaCO_3$ while the pH varied between 2,5 and 3,5.

The objective of this study was to determine the effect of different ratio's of H_2O_2/O_3 on colour removal. At the time of this study, colour removal at the main plant (coagulation, settling, filtration) was well achieved resulting in a final water colour of less than 20 mg pt/ℓ. As it was initially planned to use final water as raw water to the pilot plant, the experiment was changed in order to treat raw water for colour removal. Although this would have resulted in very high ozone dosages to be used, at least the effect of different PEROXONE dosages to the water, could be monitored. The pilot plant was operated in an on/off mode where sufficient time was allowed (5 times the retention time) to rid the plant of any effects of the previous experiment. The pilot plant was first operated at different ozone dosages to investigate the extent of colour removal. Thereafter the plant was operated continuously on an ozone dosage of 24 mg/ℓ reacted. (The transfer efficiency of the column at this ratio was determined to be about 80%.) After sufficient treatment, hydrogen peroxide was added to the process in a H_2O_2/O_3 mass ratio of 0,1, and after treatment the process was again switched to only ozone treatment. Allowing sufficient time to rid the system of the H_2O_2 and measuring the effectiveness of only ozone oxidation, H_2O_2 was again added, this time in a ratio of 0,3. This treatment (on/off) was continued while 3 samples were taken and analysed at each treatment stage. The results of this experiment is shown in Tables 4.1 and 4.2.

Table 4.1 : Effect of ozone on colour removal - Cape Brown Water

Ozone dosage (mg/ℓ)	Colour (mg Pt/ℓ)	
	Raw water	Treated water
10,4	412	361
24	443	326
36,8	434	253
49,6	438	137

Table 4.2 : Effect of H_2O_2/O_3 ratio on colour removal (ozone dosage of 24 mg/ℓ)

$\frac{H_2O_2}{O_3}$ ratio	Colour (mg Pt/ℓ)			Removal % (PEROXONE)
	Raw Water	Ozone	PEROXONE	
0	452	326	—	27,9
	468	343	—	26,7
	482	357	—	25,9
0,1	481	368	412	23,5 (14,3)
	486	361	409	25,7 (15,8)
	472	347	400	26,5 (15,9)
0,3	476	352	388	26,1 (18,5)
	451	336	365	25,5 (19,1)
	448	342	367	23,7 (18,1)
0,5	441	350	360	20,6 (18,4)
	455	348	362	23,5 (20,4)
	464	349	364	24,8 (21,6)
0,7	457	342	362	25,2 (20,8)
	456	339	359	25,6 (21,3)
	457	347	367	24,1 (19,7)
0,9	468	342	391	26,9 (16,4)
	458	345	380	24,7 (17,0)
	448	346	380	22,7 (15,1)

Figures 4.1 and 4.2 show these results graphically.

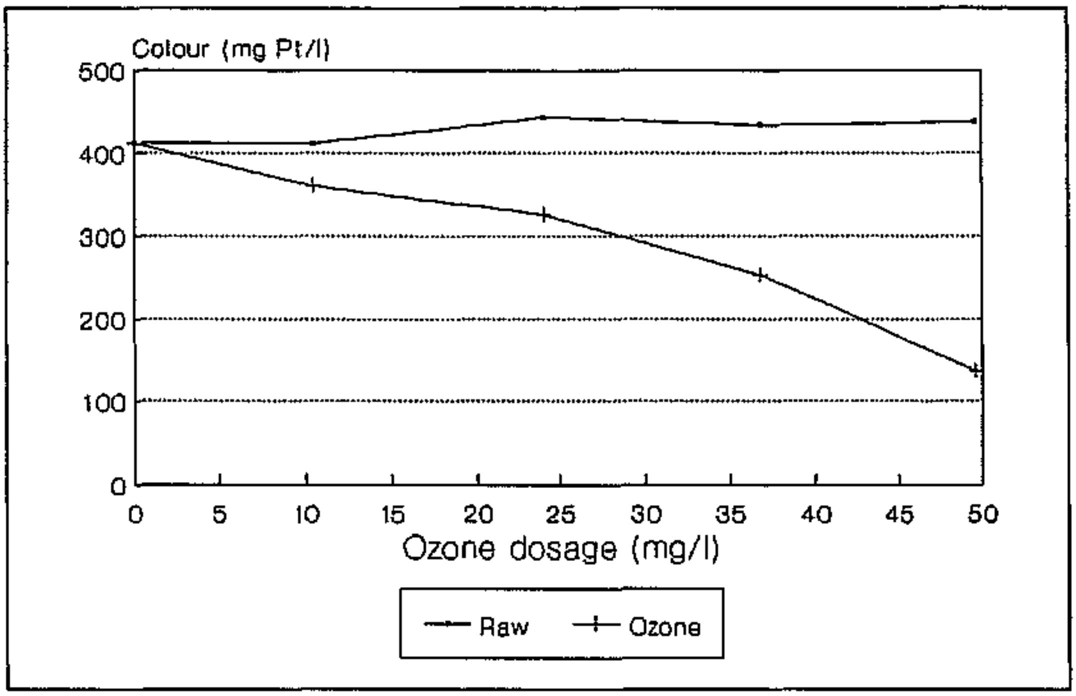


Figure 4.1 : **Colour removal by ozone at Kleinbrak Water Treatment Plant**

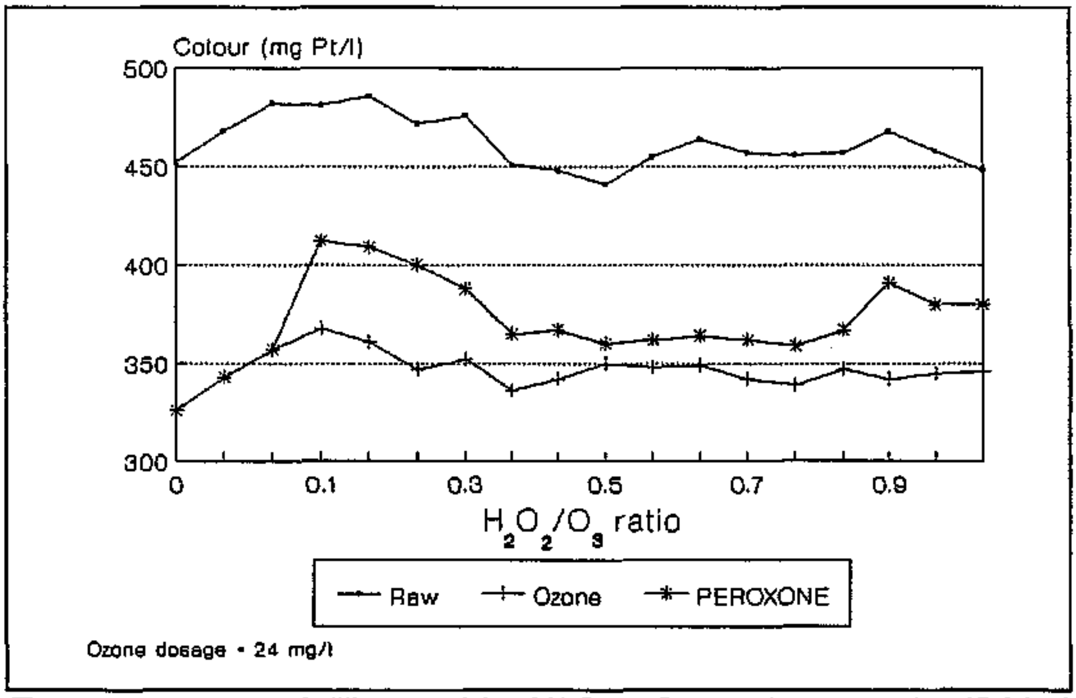


Figure 4.2 : **Effect of different ratio's of H_2O_2 to O_3 on colour removal at Kleinbrak Water Treatment Plant**

From Figure 4.1 it can be seen that colour removal with ozone takes place linearly with an ozone demand of about 0,19 mg O_3/mg Pt/ℓ. Figure 4.2 shows that the addition of H_2O_2 to the ozone process results in a lower efficiency in colour removal, supporting the fact that colour is removed via the direct ozone reaction. It is however witnessed that an increase in H_2O_2/O_3 ratio leads to better colour removal with an optimum at a ratio of 0,5 - 0,7. Further increase in the ratio above this optimum is detrimental to the process and again lower the colour removal efficiency. This indicates that at high H_2O_2/O_3 ratio's the H_2O_2 might aid as an OH radical scavenger.

4.2 Umgeni Water

This study was conducted at the Wiggans Waterworks in Durban. The equipment used as described in section 4.1 was used. The objective of this study was to determine the effect of different ratio's of H_2O_2/O_3 on the removal of organic compounds in the water. The parameter used for monitoring this effect was dissolved organic content (DOC) measured in mg/ℓ. At the time of the study the raw water had very little algae and the highest chlorophyll a content was 1,6 mg/ℓ as can be seen from Table 4.3.

The ozone dosage was increased from 1 to 3 mg/ℓ and samples taken from the raw and treated water to be analysed for DOC, algal content as well as alkalinity. These results are shown in Table 4.3 (raw water values in brackets).

Table 4.3 : Effect of H_2O_2/O_3 ratio on organic content - Umgeni Water

Ozone dosage (mg/ℓ)	H_2O_2/O_3 ratio	Alkalinity (mg/ℓ as $CaCo_3$)	DOC (mg/ℓ)	Chlorophyll a (mg/ℓ)
1	0	58,5 (59,5)	2,2 (2,0)	1,48 (0,3)
	0,2	57,5 (55,5)	2,3 (2,4)	0,79 (0,26)
	0,4	53 (57,5)	2,2 (2,7)	0,53 (0,0)
	0,6	58 (57)	2 (2,1)	1,38 (0,28)
	0,8	58,5 (58,5)	2,4 (2,6)	0,53 (0,82)
1,5	0	58 (58,5)	2,8 (2)	0,69 (0,34)
	0,2	54 (53)	2,3 (2,4)	0,56 (0,42)
	0,4	59 (58)	2,5 (2,4)	0,54 (0,32)
	0,6	65 (59,5)	2,6 (2,1)	0,77 (0,92)
	0,8	60 (57)	2,7 (2,6)	0,27 (0,84)
2	0	56 (45)	2,3 (1,9)	0,28 (0,25)
	0,2	49,5 (57)	1,9 (2,6)	0,67 (0,3)
	0,4	58,5 (58,5)	2,2 (2,1)	0,21 (0,29)
	0,6	58 (57,5)	2 (2,2)	0,25 (0,53)
	0,8	58,5 (57)	2,5 (2,7)	0,26 (1,6)
2,5	0	58 (58,5)	1,6 (2,1)	0 (0,32)
	0,2	55 (57)	1,8 (2,5)	0,26 (0,27)
	0,4	55,5 (57,5)	2,6 (2,1)	0,24 (0,21)
	0,6	59 (58,5)	2,4 (2,1)	0,2 (0,38)
	0,8	58,5 (59)	2,4 (2,6)	0,26 (0,84)
3	0	51 (57,5)	1,7 (2,3)	0,26 (0,53)
	0,2	57 (58)	2 (2,6)	0,57 (0,53)
	0,4	59 (54,5)	2,4 (2,1)	0,34 (0,26)
	0,6	59,5 (59)	2,4 (2,1)	0,26 (0,28)
	0,8	59 (59)	2,7 (2,6)	1,03 (0)

Figures 4.3 to 4.10 show the results graphically.

The results indicate that the addition of hydrogen peroxide to ozone does not have any effect on the removal of organic content (measured as DOC) from the water.

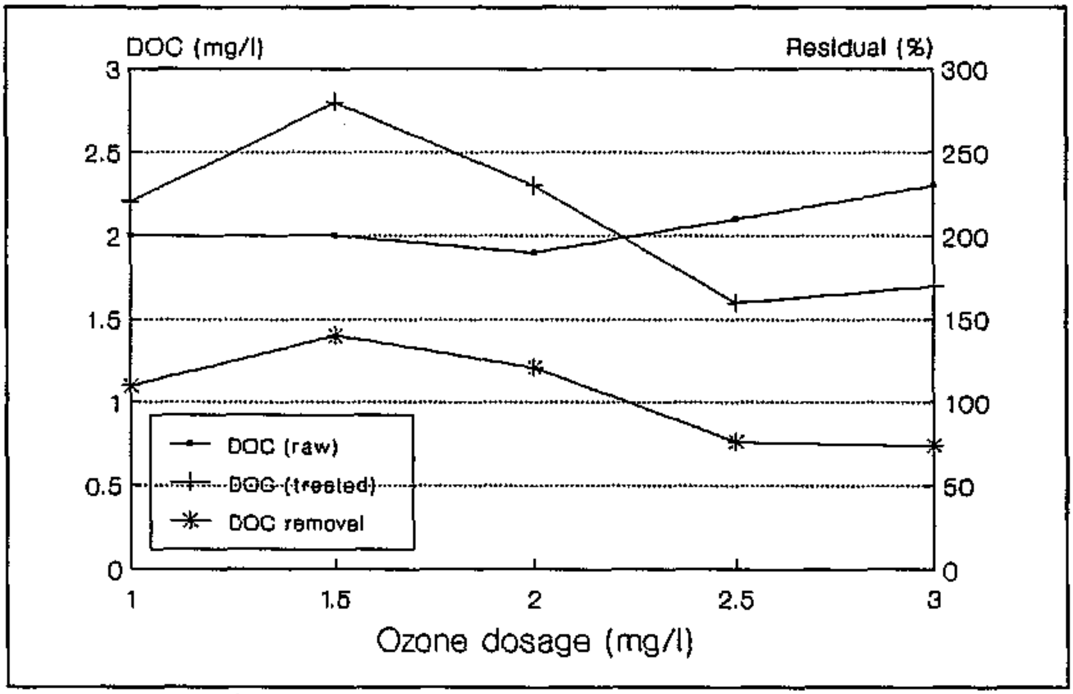


Figure 4.3 : DOC removal with ozone

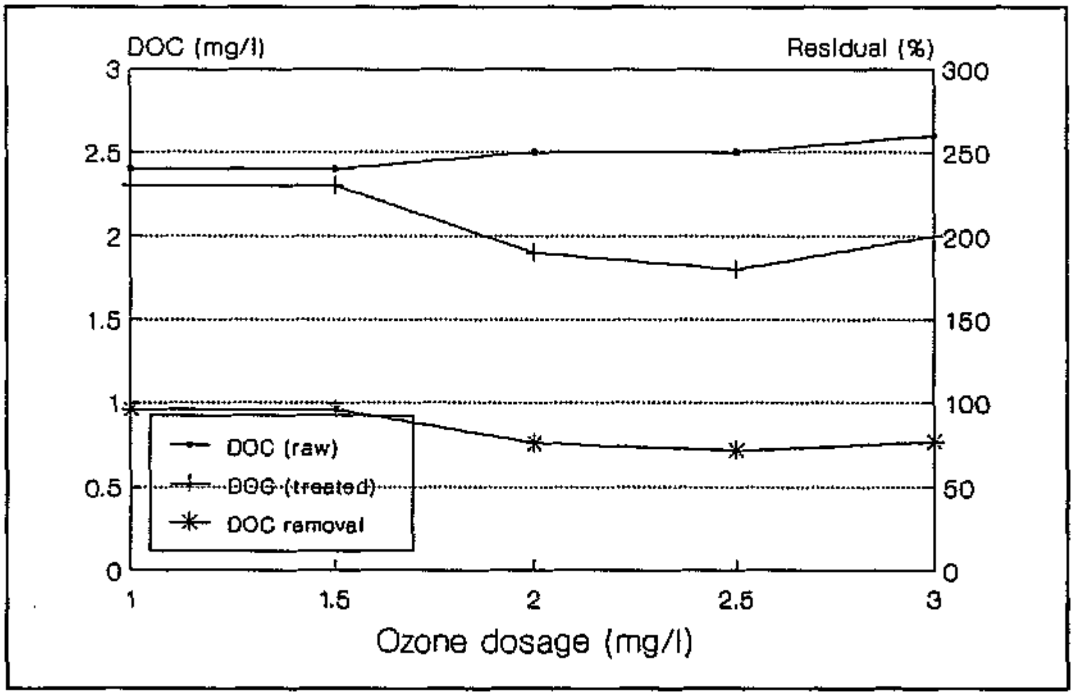


Figure 4.4 : DOC removal with PEROXONE (ratio H_2O_2/O_3 = 0,2)

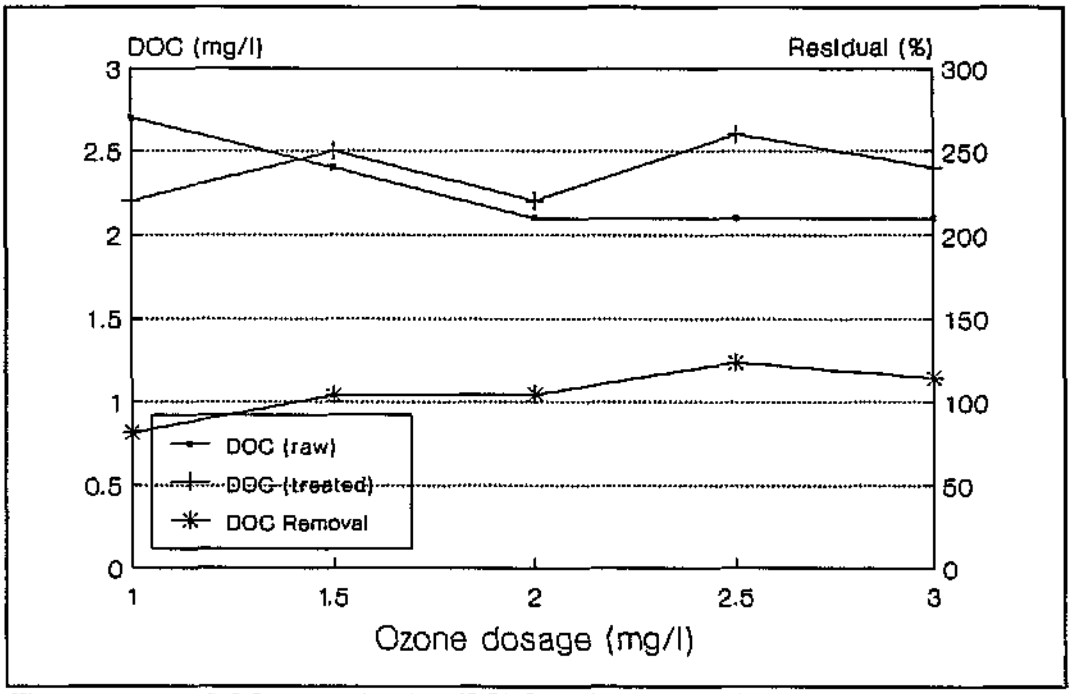


Figure 4.5 : DOC removal with PEROXONE (ratio $H_2/O_2/O_3$ = 0,4)

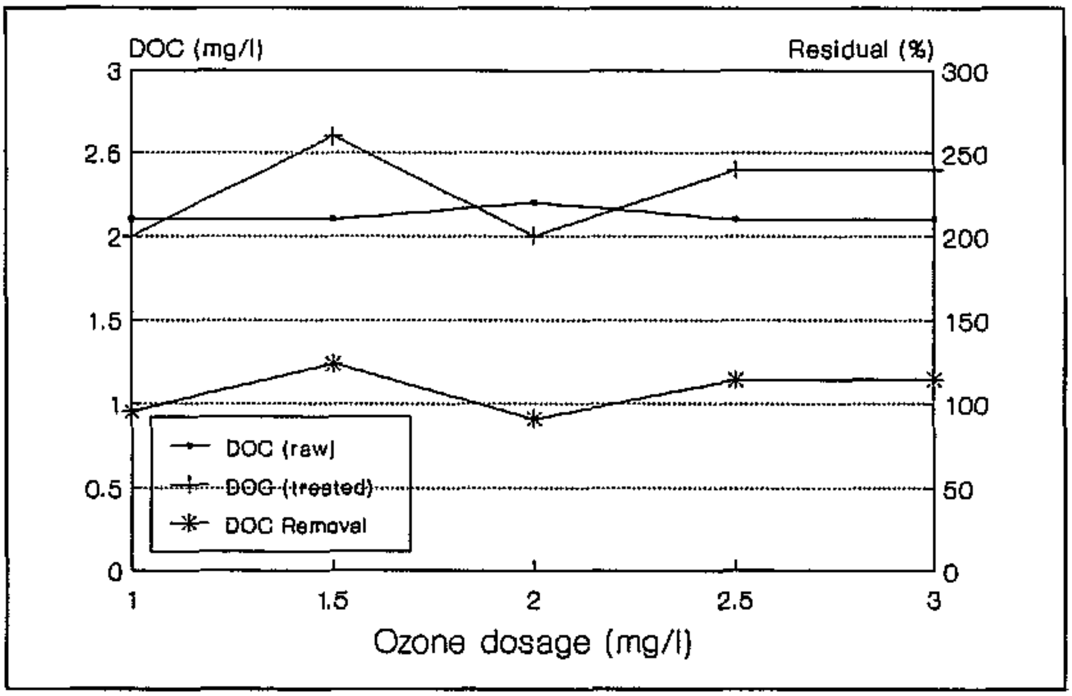


Figure 4.6 : DOC removal with PEROXONE (ratio H_2O_2/O_3 = 0,6)

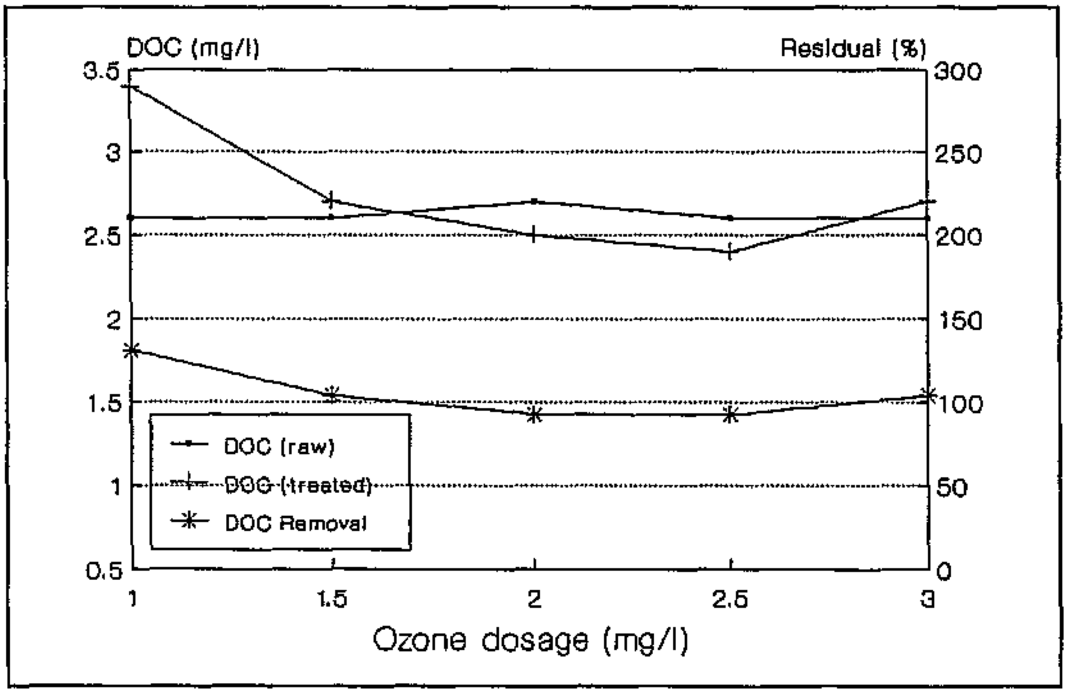


Figure 4.7 : DOC removal with PEROXONE (ratio $H_2/O_2/O_3$ = 0,8)

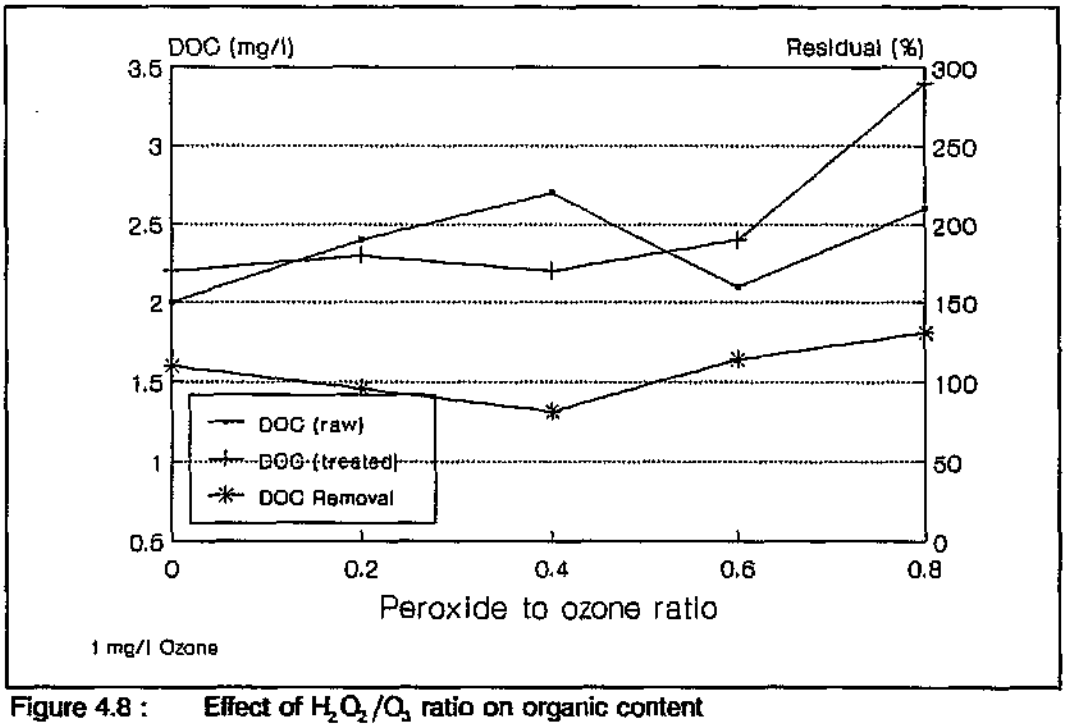


Figure 4.8 : Effect of H_2O_2/O_3 ratio on organic content (1 mg/ℓ ozone)

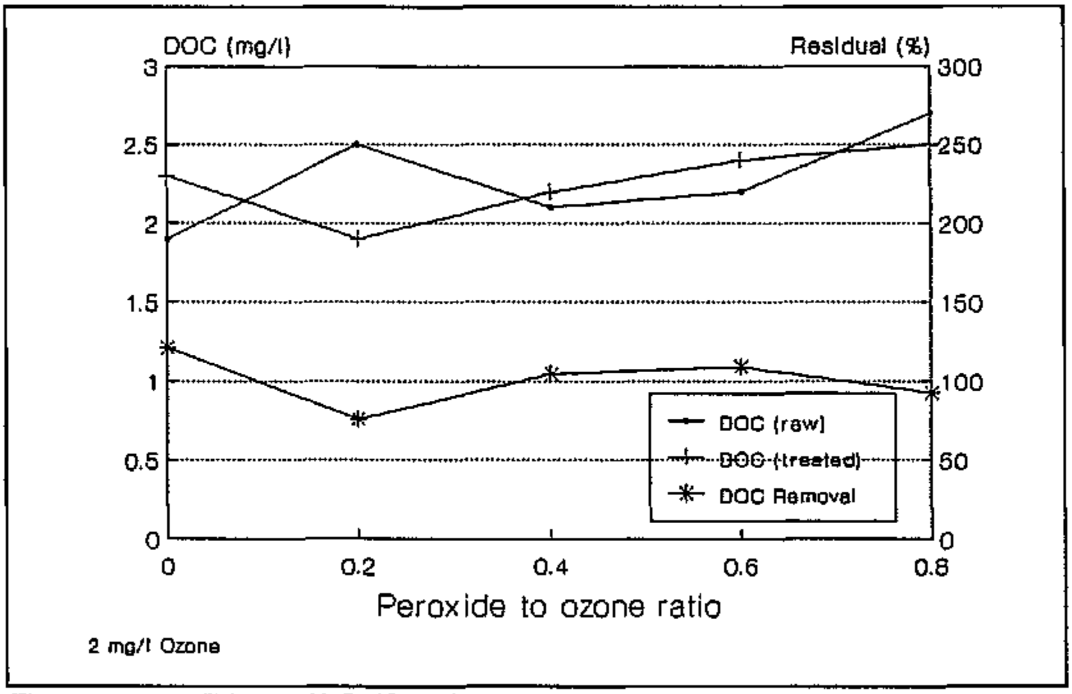


Figure 4.9 : Effect of H_2O_2/O_3 ratio on organic content (2 mg/ℓ ozone)

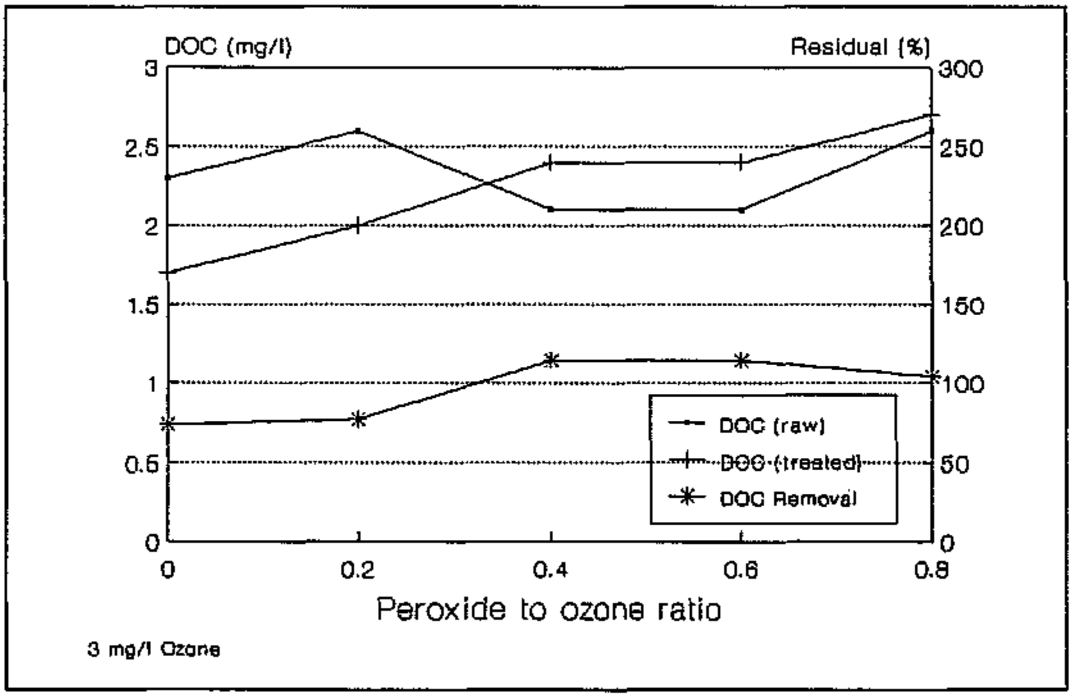


Figure 4.10 : Effect of H_2O_2/O_3 ratio on organic content (3 mg/ℓ ozone)

No pattern could be observed with the alkalinity values where, in some cases, a decrease in alkalinity after treatment is observed and in other cases an increase. The same goes for the chlorophyll a values which cannot be explained.

CHAPTER 5 : FULL SCALE STUDY

5.1 Western Transvaal Regional Water Company

The Western Transvaal Regional Water Company uses ozone primarily for the oxidation of manganese in the raw water. During September 1993 several tests were performed in order to determine whether the addition of H_2O_2 to the ozone process could have a beneficial effect on organic removal in the water.

5.1.1 Results

The results of this study are shown in Appendix 1.

Flocculation tests were conducted on the water prior to oxidation as well as after oxidation in order to determine the effect of ozone and PEROXONE on flocculation characteristics. These tests were also conducted on the water treated by UV and UV/H_2O_2. Figures 5.1 -5.6 shows the results of these tests

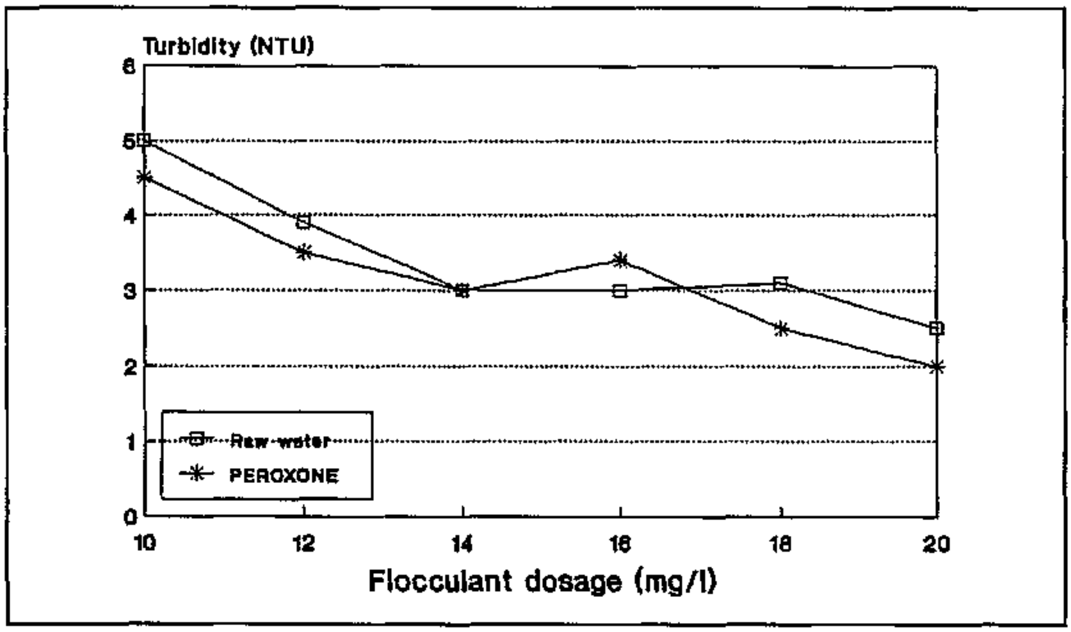


Figure 5.1 : Flocculation tests - day one (15/09/93)

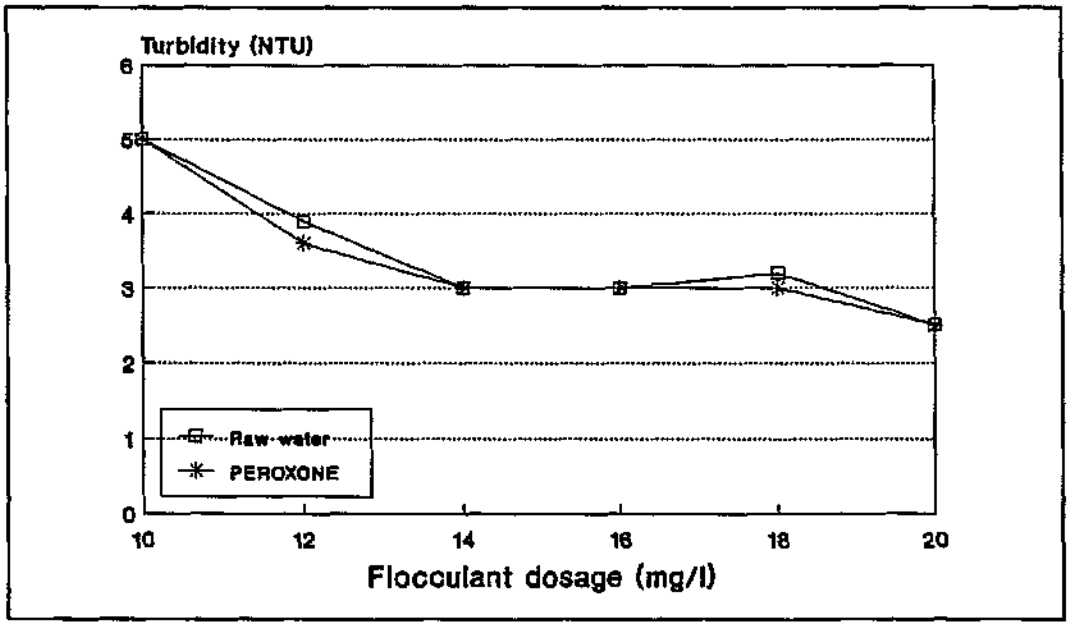


Figure 3.2 : Floculation tests - day two (16/09/93)

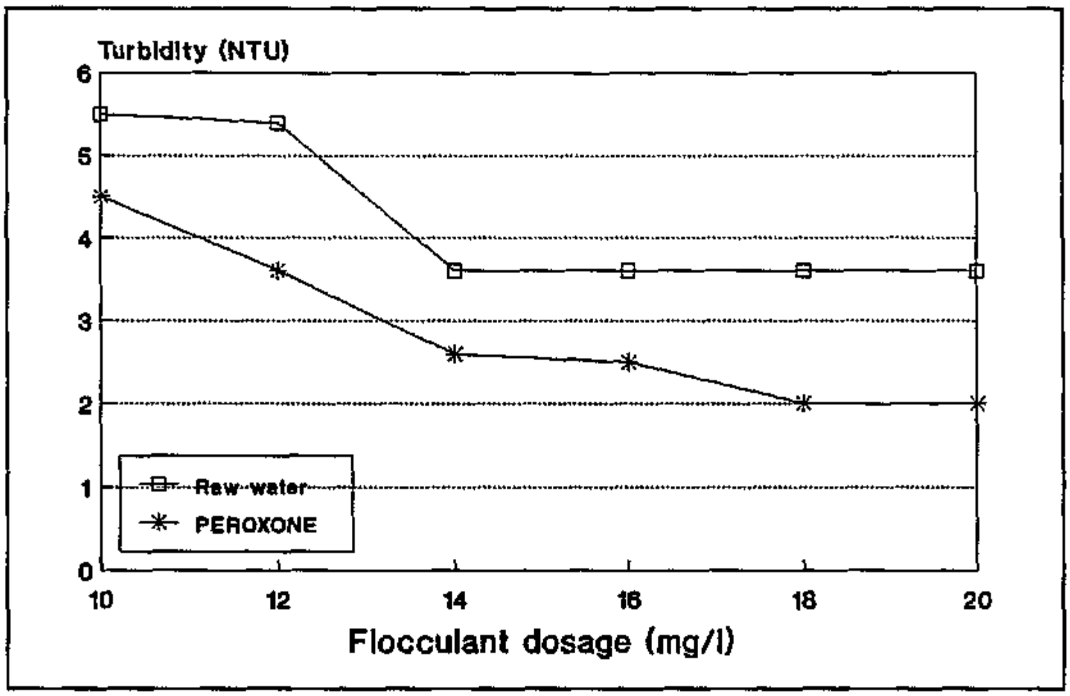


Figure 5.3 : Floculation tests - day three (17/09/93)

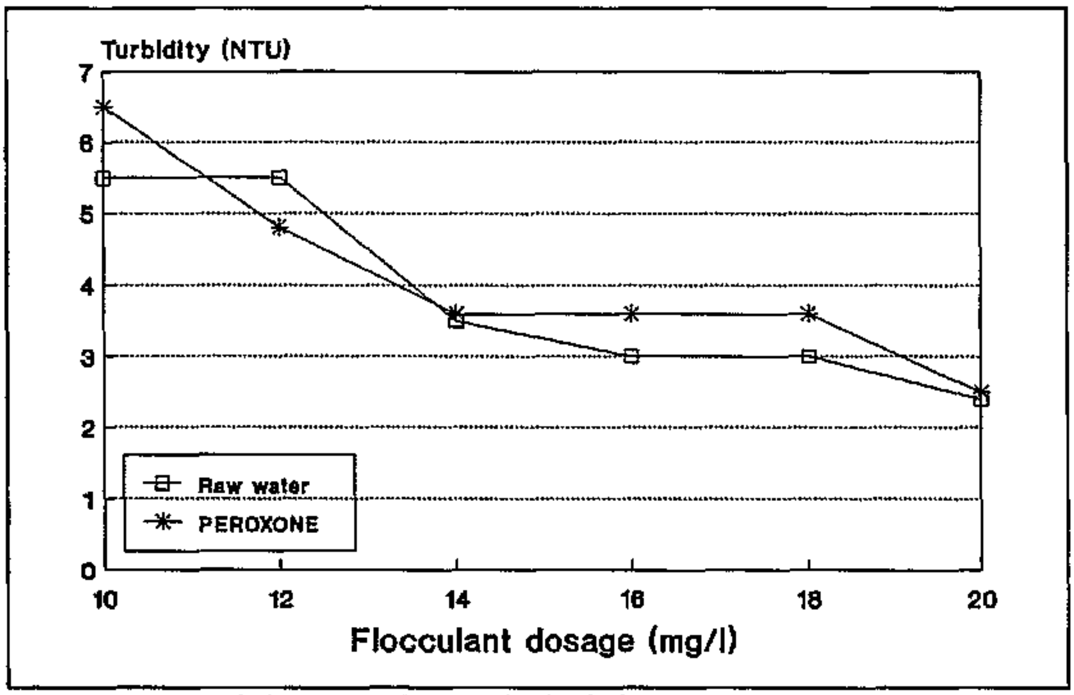


Figure 5.4 : Flocculation tests - day four (20/09/93)

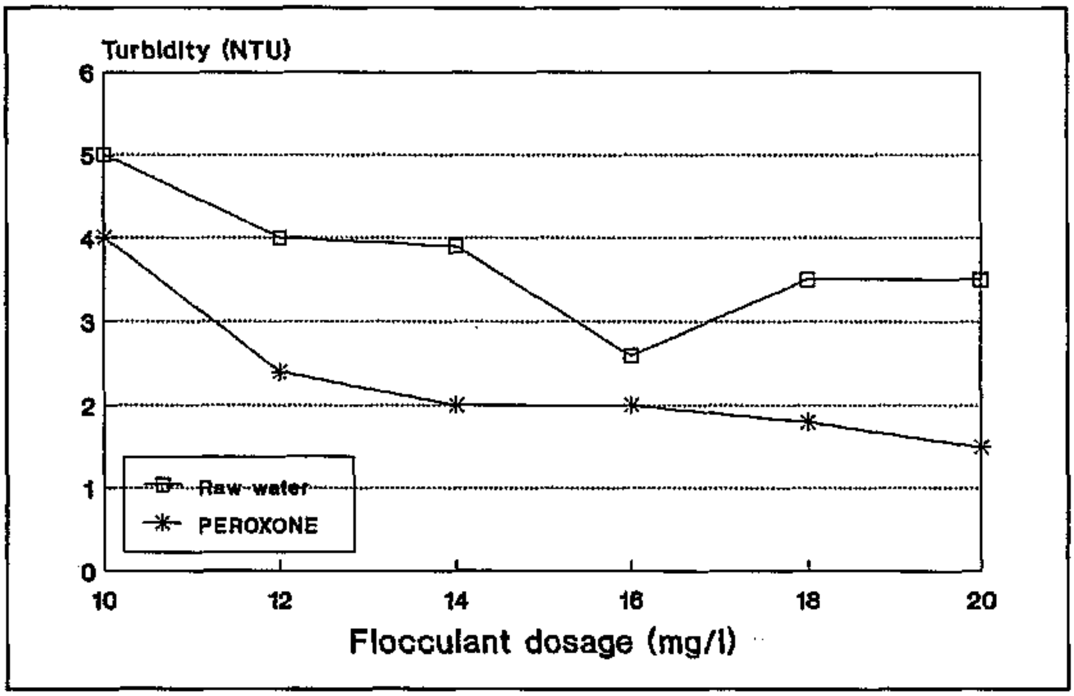


Figure 5.5 : Floculation tests - day five (21/09/93)

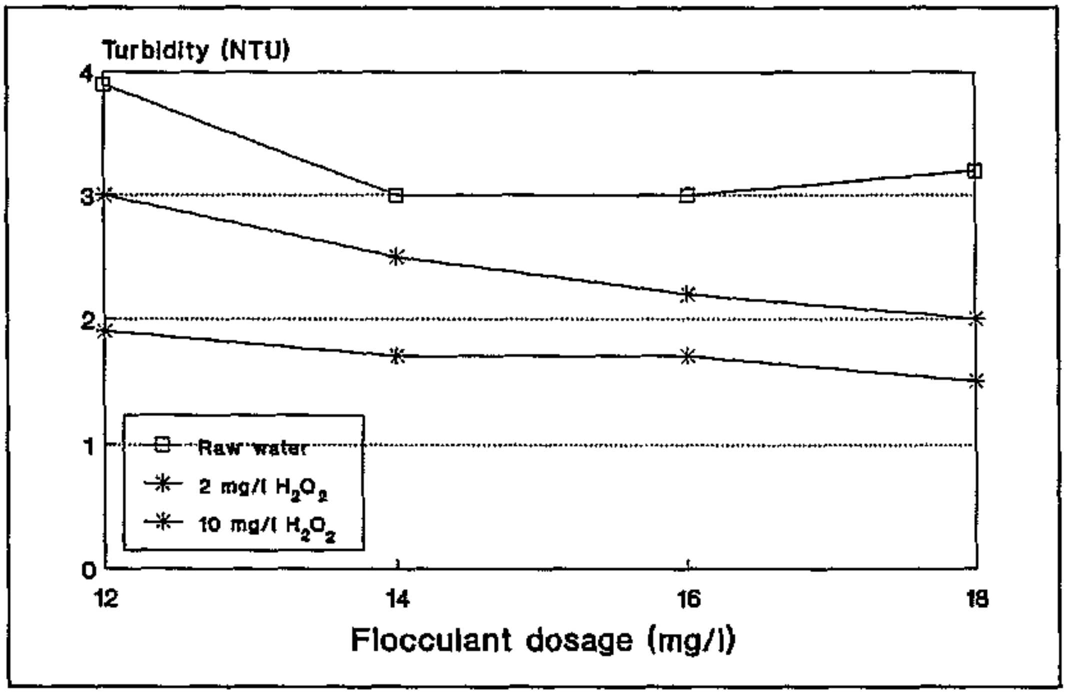


Figure 5.6 : Flocculation tests - with UV

Although some results show that the addition of ozone can result in less coagulant used while obtaining a similar quality water than when raw water is flocculated at high flocculant dosages (see figures 5.3 and 5.5), these results are not repetitive.

Figures 5.7 - 5.10 show the results of the tests at this plant graphically. Figures 5.11 and 5.12 show the amount of organic material left in the water after oxidation with UV and the combination of UV and hydrogen peroxide (expressed as % DOC and TOC relative to the DOC and TOC concentration before oxidation). Again the fact that more organic material is left in the water after oxidation than before can be explained with the fact that algae in the water are broken up by the oxidant with the result that these organic material are released into the water. No conclusion can be made from these results.

Figure 5.9 shows that removal of age is a function of UV dosage and that the addition of hydrogen peroxide to the water have little influence on the effectiveness of this process.

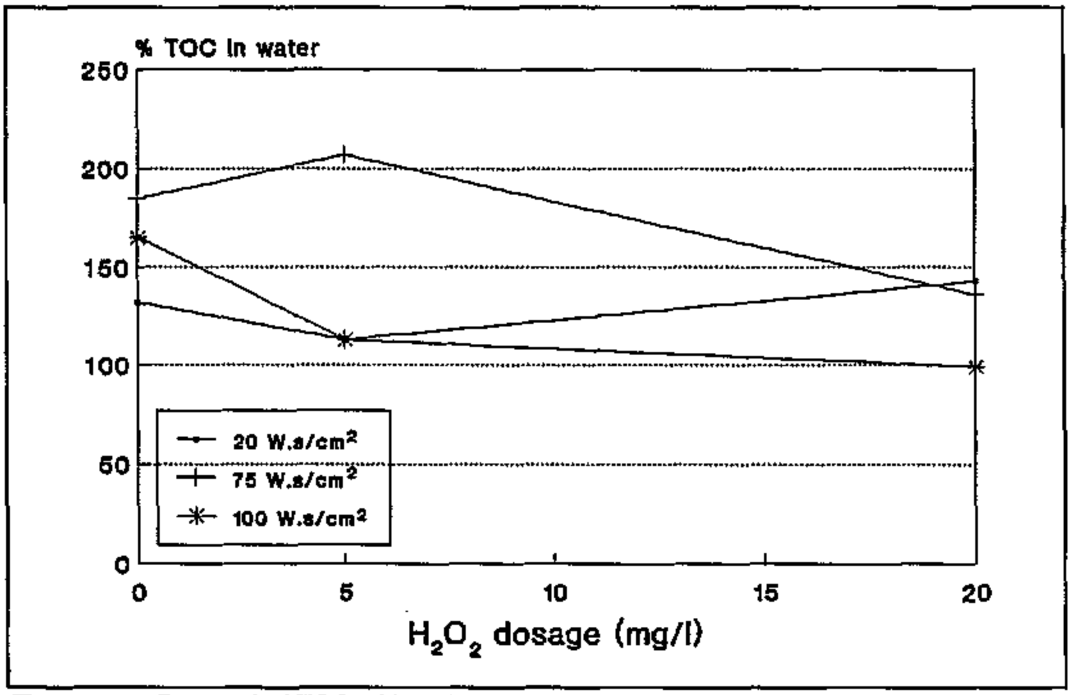


Figure 5.7 : Removal of TOC with UV

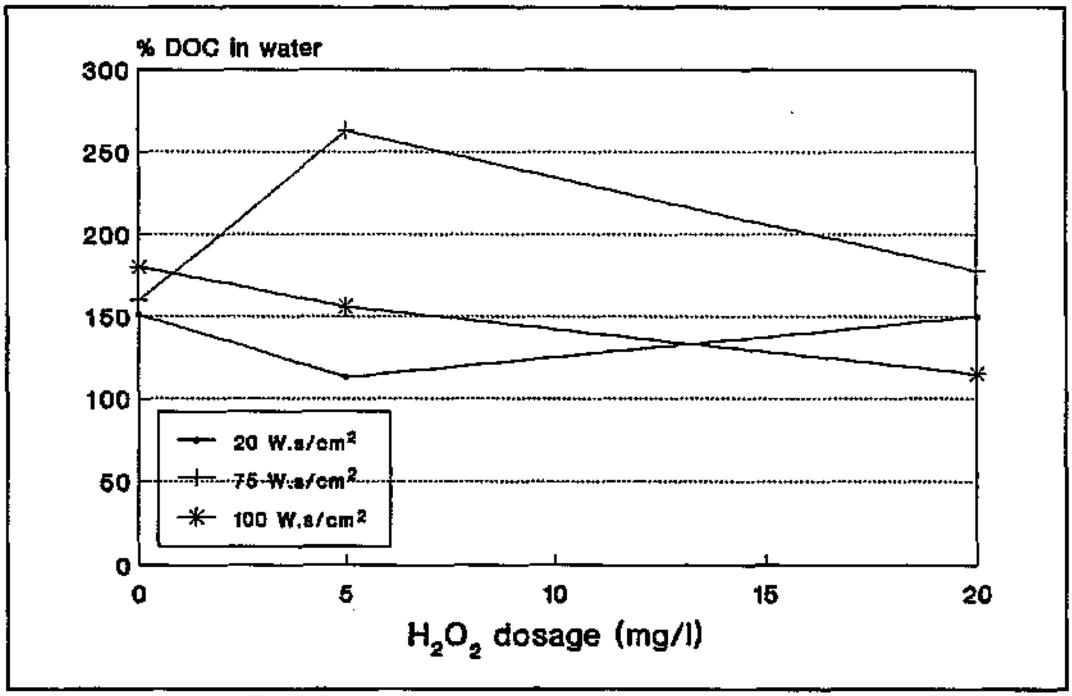


Figure 5.8 : Removal of DOC with UV

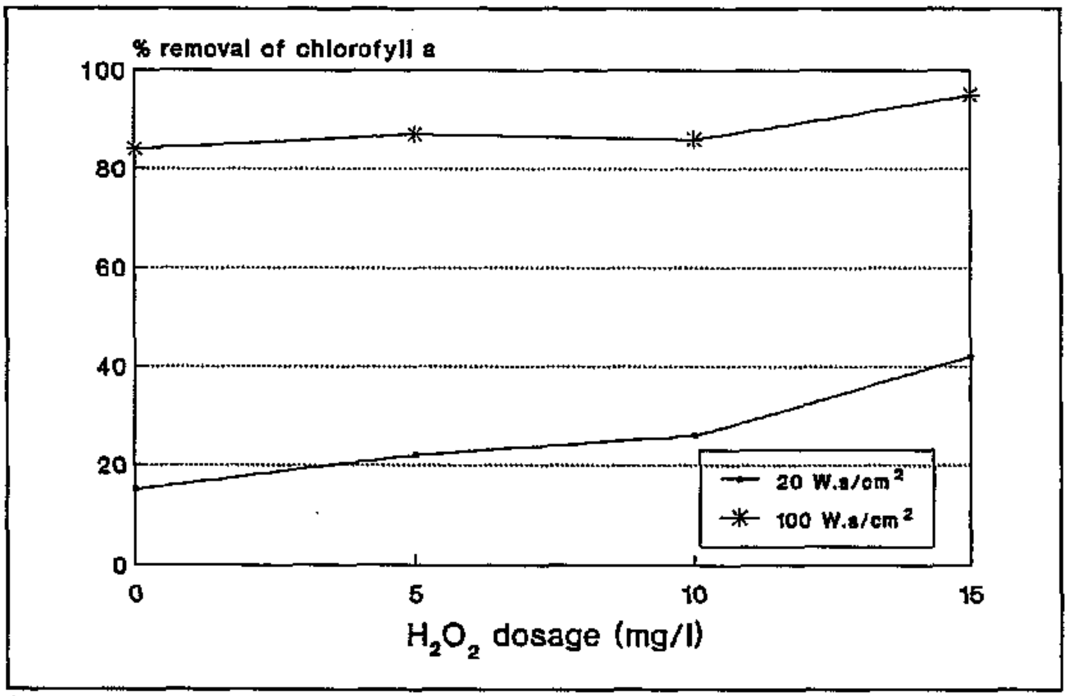


Figure 5.9 : Removal of algae with UV

Figure 5.10 compares the effectiveness of ozone and PEROXONE on the removal of TOC, DOC and chlorophyll a throughout the plant. It is clear that ozone performed better than PEROXONE with regard to removal of organic content in the water. It was also found that, generally, less trihalomethane formation took place when ozone was used as single oxidant than when PEROXONE was used. From these tests, it is clear that PEROXONE as oxidant have no benefit over the use of ozone as single oxidant for this type of water.

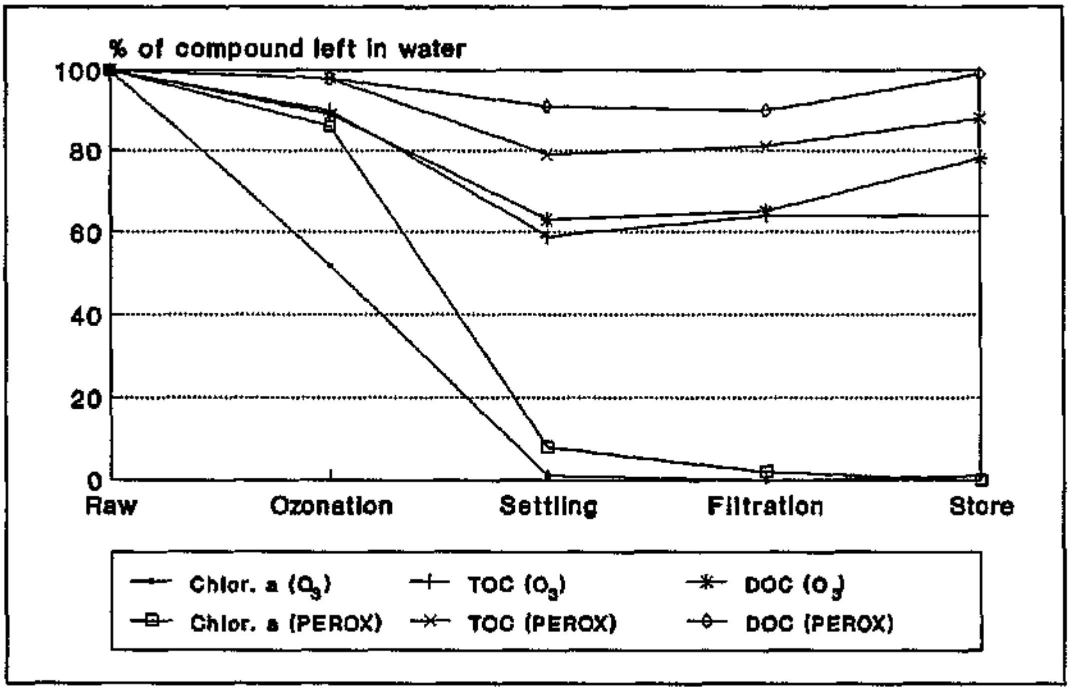


Figure 5.10 : Comparison of ozone and PEROXONE performance through the plant

CHAPTER 6 : COST IMPLICATIONS

Ozone is often considered to be expensive. This is caused by the difficulty to compare a chemical, ozone, which is produced on site and requires a plant investment with chemicals, such as chlorine, which are bought as such and delivered to the plant. It is also influenced by the fact that the economy of utilizing ozone is not easily quantified. Because of this the difference of the unit cost per m^3 of ozonated water or per gram of ozone produced can be considerable between the contract specifications and the figures appearing on the yearly balance sheet under the headings : kW-h consumed, maintenance, operating and maintenance personnel.

Because of the many variables playing a role in the estimation of the costs involved such as the cost of electricity, cost of cooling water, interest and inflation rates, and the utilization factor of the generator to name but a few, each attempt to estimate the cost effectiveness of ozone must be seen in the context of its application.

Geering (1989) put forward production costs of ozone (excluding investment cost) of between 0,6 and 1 US cents/g of ozone produced. This was based on an ozonation plant operating continuously at maximum with electricity costs of 10 cents per kW-h and cooling water costs of 67 cents per m^3. This is about two to three times higher than the cost found elsewhere in practice (Schulhof, 1989).

In a study by Schulhof (1989) the ozonation costs associated with three water treatment plants in France was calculated. Ozone used in these plants is for oxidation and disinfection purposes and air is used as the feed gas. For a 100 % use factor and including operating, investment and maintenance cost, a total ozonation cost of 0,62 cents per gram ozone produced was calculated. With an average dosage of 3 mg/ℓ of ozone, the cost of ozonation was reported as 3,62 cents/m^3 water produced.

In a very well documented study by Lepage (1989), the economics of operating the ozonation facility at the water works in Monroe, Michigan, are reviewed after ten years of operation. Ozonation is employed here for the destruction of objectionable odours and tastes. During the ten years of operation, the average cost for ozone generation was 1,02 cents/g ozone and with an average dosage of 1,23 mg/ℓ, the cost for treating the water was 1,27 cents/m^3 water treated. This may appear high at first glance but in the study all expenses chargeable against the ozonation system was considered. This includes all overhead and operating expenses. Frequently, in the preparation of cost analyses, major items such as debt retirement, insurance, and others are overlooked or ignored in order to portray favourable operating costs. In this study, overheads such as debt retirement and insurance, alone translates to just over half of the monies spent for the ozonation system in the ten year period. Thus, in his study, no attempts were made to temper actual costs and amounts shown in his report are actual paid out dollars.

A host of beneficial side effects of ozonation occur simultaneously with taste and odour destruction at no additional cost (Lepage, 1989). Many impact directly and favourable on operating economics through savings in treatment chemicals, energy labour and service water. Others, while easily recognized, are of a more subtle economic advantage for example in the destruction of intermittently occurring cyanides.

To put ozonation in perspective, Lepage calculated that ozonation added only $ 1-05 to a three month water bill of the consumer.

Wunsch and Darpin (1989), give the characteristics of ozone generation systems which have to be taken into consideration in evaluating the cost effectiveness of ozone generation systems. This include aspects such as maintenance costs, cooling water consumption, electricity costs, etc. In their paper, a detailed way of calculating the total specific annual costs of an ozonation system is shown. These calculations are summed up in Appendix 2 (Adapted for RSA Rand).

Table 6.1 Cost Analyses : Production of ozone from air (Wunsch and Darpin, 1989)

FORMULAS	$TAC = SCC + SOC$ $SCC = \frac{(J_o + \Delta J_o)}{M}(1 + \frac{i+e}{100})^b ANF + \frac{U}{M}$ $SOC = (X.E_s + Y.W_s)EUP$ $ANF = \frac{q^n(q-1)}{q^n - 1}$	
SYMBOL	DESCRIPTION	UNITS
TAC	Total annual costs	R.h/kg O_3.a
SCC	Specific capital and fixed operational costs	R.h/kg O_3.a
SOC	Specific operational costs	R.h/kg O_3.a
E_s	Specific energy consumption	kW.h/kg O_3
J_o	Capital investment	R
U	Annual maintenance costs	R/a
W	Cooling water consumption	m^3/kg O_3
X	Cost of electricity	R/kW.h
Y	Cost of cooling water	R/m^3
b	Construction period	a
i	Interest rate	% p.a.
e	Inflation	% p.a.
n	Depreciation period	a
t	Tax on investment	% p.a.
v	Investment related insurance	% p.a.
ANF	Annuity factor	
EUP	Equivalent utilization period	

When ozone is generated from oxygen, higher investments may be necessary which must be taken into account in the specific capital and fixed operational costs. Specific operational costs is also expanded to :

$$SOC=(X.E_s+Y.W_s+Z.O_s)EUP$$

where : O_s = Specific oxygen consumption (kg/kg O_3)
Z = Cost of oxygen (R/kg)

By using this method, it is possible to calculate the total annual cost of an ozonation system. By making some assumptions it is calculated that, in South-Africa, the cost of generating 1 kg of ozone from air will be approximately R13.86/kg and with an ozone dosage of 1.3 mg/ℓ, this will result to 1,8 cents/m^3 water treated. Similarly, for ozone generation from oxygen, the cost of generating 1 kg of ozone will be approximately R13-17/kg and with an ozone dosage of 1.3 mg/ℓ, this will result to 1,7 cents/m^3 water treated. These calculations and assumptions are shown in Appendix 1.

The following two examples shows the difference in cost for treatment of a specific water :

- Removal of colour from 50 mg/ℓ to 20 mg/ℓ - dosages as determined in section 3.3 used.
- Ozone at 4.5 mg/l @ R13.86/kg = 6.2 c/m^3
- PEROXONE at 6.8 mg/l O_3 and 2.7 mg/l H_2O_2 @ R6/kg peroxide = 11 c/m^3
- Chlorine at 10.5 mg/l @ R3.70/kg = 3.9 c/m^3
- Chlorine dioxide at 1.8 mg/l @ R22.50/kg = 4.05 c/m^3

It is seen that although chlorine proves to be cheaper than the other oxidants, the use of chlorine dioxide and ozone might be considered if aspects such as health and ease of operation is taken into account

- Removal of DBS from 1.7 mg/ℓ to 0.5 mg/ℓ - dosages as determined in section 3.2 used.
- Ozone at 14.5 mg/l @ R13.86/kg = 20.1 c/m^3
- PEROXONE at 8 mg/l O_3 and 3.2 mg/l H_2O_2 @ R6/kg peroxide = 13 c/m^3
- Chlorine at 15 mg/l @ R3.70/kg = 5.6 c/m^3
- Chlorine dioxide at 1.1 mg/l @ R22.50/kg = 2.5 c/m^3
- Hydrogen peroxide at 22 mg/l @ R6/kg = 13.2 c/m^3
- UV at 25 Ws/cm^2 @ 5.6 cents/m^3 for every Ws/cm^2 = 140 c/m^3
- UV at 8 Ws/cm^2 and peroxide at 5 mg/ℓ = 52 c/m^3

It is clear that UV at high dosages is not cost effective and that the oxidant of choice for this type of water must be chlorine dioxide.

In evaluating an oxidant for a specific task, the following issues therefore need to be investigated :

- Can this specific oxidant do the job ?. Will this chemical be able to perform under all operating conditions, taking into account variances in water quality such as concentration, temperature, pH, etc ?
- Are there any side effects (negative or positive) ?. This can include aspects such as health implications, possible aid in flocculation, removal of other non-targeted compounds, etc.
- Is this chemical cost effective ?. This is probably the most important aspect. Realizing the difficulty to compare a chemical such as chlorine with a physical process such as UV, care should be taken to compare oxidants on an even basis.
- Operational aspects. Other factors equal, one should investigate operational aspects involved with the use of an oxidant. The use of UV certainly seems very elegant where no toxic chemicals need to be transported leading to safer working conditions and it is environmentally friendly.

CHAPTER 7 : GUIDELINES AND CONCLUSIONS

Interest in ozonation has increased in recent years, primarily as a result of concerns about the formation of chlorination by-products such as THMs which are produced during chlorination of drinking water. In addition to its use as a disinfectant, ozone can be used for taste and odour control, decolorization and the oxidation of harmful compounds in water.

The addition of hydrogen peroxide to the ozone process (the so called advanced oxidation process) has also been investigated by numerous researchers and has led to the implementation of this process in several facilities in Europe. As the ozone process is almost standard practice in Europe, this addition of peroxide had minimal cost implications, however, the advantage gained by the process is claimed to be significant, especially where PEROXONE is used in the destruction of pesticides and other micropollutants. Before the use of ozone and PEROXONE can be promoted in South-Africa based on overseas experience, research in the ozonation and peroxidation technologies should be conducted.

This project aimed on providing guidelines for the use of ozone and PEROXONE on South-African surface waters. Several issues were investigated, a discussion of the most important results follows :

Colour removal

Generally it was found that colour removal was obtained via the direct ozone reaction. It was however seen that colour removal could be accomplished with hydroxyl radical oxidation as is witnessed with the addition of hydrogen peroxide to UV light. Results also showed that chlorine and chlorine dioxide could effectively remove colour whereas the use of hydrogen peroxide was ineffective in oxidizing humic and fulvic acids.

Taste and odour removal

Results indicate that oxidation of geosmin and MIB took place following the radical oxidation pathway. This is clearly seen where the addition of hydrogen peroxide to ozone and UV led to enhanced removal of the compounds. In contrast to this, the use of conventional oxidants such as chlorine, chlorine dioxide and hydrogen peroxide were not effective in removal of these compounds. The use of Ultra Violet irradiation showed that these compounds absorb UV light and can undergo oxidation using this technique.

THM formation

In terms of actual trihalomethane formation, the use of ozone, PEROXONE and chlorine dioxide are preferable over the conventional use of chlorine. Evaluating the tendency of THM formation after oxidation; i.e. giving an indication of the amount of oxidation that occurred, it is seen that results differ for the different waters. At the coloured waters, where ozone treatment was shown to be more efficient than PEROXONE, a higher formation potential was realized which suggests that ozone oxidises the organic compounds such that more THM's are produced after chlorination than with PEROXONE. At the Western Transvaal and Umgeni Waters no difference in performance for these two oxidants could be seen.

Removal of harmful organics

The difference in oxidation behaviour of phenol and DBS indicates that some prediction in whether a specific compound will be susceptible to radical pathway oxidation can be made. It is seen that where the direct oxidation reaction prevails (with phenol), the compound doesn't absorb UV light, is not removed with hydrogen peroxide and effective oxidation with chlorine and chlorine dioxide takes place at low and high pH values. This situation is reversed when the radical pathway oxidation mechanism is preferred. It is seen with DBS that the compound reacts favourably to UV irradiation and that hydrogen peroxide at high pH values oxidises the compound. In contrast with phenol, very little removal takes place when chlorine or chlorine dioxide is used at low pH values.

Effect of alkalinity

The presence of scavenging compounds such as carbonate ions clearly had a detrimental impact on the radical oxidation process. It was seen that an increase in alkalinity in the coloured waters reduced the effectiveness of PEROXONE in the removal of colour.

Impact on flocculation

In general it was seen that ozone had no impact on improving flocculation. It was in fact observed upon ozonation of Wilge river water that a detrimental effect occurred where a lower quality water was obtained after flocculation and settling than without ozonation.

Guidelines for the use of PEROXONE on South African surface waters

The use of PEROXONE in potable water treatment must have a **specific objective** such as the removal of a taste and odour compound or a pesticide. The effectiveness of this process is then only measured in terms of removal of this specific compound. The implementation of an advanced oxidation process is also dependent on the type of unit processes already installed in the treatment plant. If the treatment plant for example already employs the duty of an ozone plant or UV irradiation, the extra cost for dosing of hydrogen peroxide will be minimal.

The process must be **cost effective**. In order to perform a cost analysis it will be important to determine dosages required as well as true costs associated with the specific oxidant such as discussed in chapter 6. Dosage determination should be conducted under controlled conditions and on a typical water sample to be treated. It is important that the destruction of specific micropollutants should not be investigated in the absence of background natural organic material. Because these natural organic materials are often present at concentrations several orders of magnitude greater than the micropollutant of interest and because these radical reactions are nonselective, the effectiveness of these processes for destroying specific micropollutants in such a natural water matrix should be determined.

Attention must be given to the **health implications** associated with the use of that specific oxidant. It was seen that the use of ozone and PEROXONE produce very little if any THM's on its own, however the subsequent chlorination of the water can indeed form more THM's due to breakdown of organics into compounds susceptible to THM formation. The use of chlorine dioxide for oxidation of organics resulted in low dosages to be used, as well as low formation of THM's and looks favourable. Apart from THM formation, one should also be aware of the possible effects of bromate formation when ozone is used as oxidant and/or disinfectant. Although this issue is still debatable, it cannot be disregarded.

Although the use of UV and the combination thereof with hydrogen peroxide was also investigated, its commercial use can be limited due to the high dosages required. Where UV is normally used for disinfection purposes with dosages in the region of 40 mWs/cm^2, the dosages needed for oxidation is several orders of magnitude more; this leads to high treatment costs.

It is therefore concluded that PEROXONE as a unit process in a water treatment plant has a niche position and is component specific. The following table can therefore be used as a guide for implementation of this process, and other oxidants, for the removal of specific pollutants:-

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APPENDIX 1

FULL SCALE STUDY RESULTS AT WESTERN TRANSVAAL REGIONAL WATER COMPANY

Table 5.1 : Raw water quality (September 1993)

Day	Time	Dissolved organic carbon (mg/ℓ)	Total organic carbon (mg/ℓ)	pH	Alkalinity (mg/ℓ $CaCO_3$)	Chlorophyll a (µg/ℓ)	Manganese (mg/ℓ)	Colour (mg Pt/ℓ)
14/9	07:00	4.67	5.72	7.78	88	63.1	0.04	150
	14:00	5.70	5.85	8.21	88	81.2	0.04	150
15/9	07:00	4.32	5.41	7.75	88	60.2	0.04	175
	14:00	4.97	6.09	8.26	86	54.0	0.09	175
16/9	07:00	5.52	6.27	7.80	84	59.2	0.05	175
	14:00	5.48	5.72	8.30	84	75.5	0.09	175
17/9	07:00	5.40	5.86	7.89	88	73.6	0.04	175
	14:00	6.23	6.88	8.16	80	66.9	0.07	175
20/9	07:00	5.62	6.36	7.51	82	43.9	0.02	175
	14:00	5.10	8.14	8.10	84	25.0	0.05	175
21/9	07:00	6.27	6.89	7.79	78	9.6	0.04	175
	14:00	5.79	5.85	7.76	82	17.0	0.11	175
22/9	07:00	4.23	4.96	7.65	86	24.8	0.05	175
	14:00	5.36	6.48	7.81	86	25.0	0.05	175
23/9	07:00	4.67	5.51	7.41	84	19.0	0.02	175
	14:00	6.24	7.60	7.44	82	20.0	0.01	175
24/9	07:00	5.03	5.77	7.50	83	26.7	0.02	175
	14:00	6.74	8.85	7.70	80	-	0.06	175

Table 5.2 : Water quality after oxidation (September 1993)

Day	Time	H_2O_2/O_3 mass ratio	Dissolved organic carbon (mg/ℓ)	Total organic carbon (mg/ℓ)	pH	Alkalinity (mg/ℓ $CaCO_3$)	Chlorophyll a (µ g/ℓ)	Colour (mg Pt/ℓ)
14/9	09:00	0.4	7.12	9.13	7.93	84		150
	10:30	0.4	6.41	6.45	7.96	84	59.2	150
	12:00	0	5.96	9.01	7.97	84		150
	13:30	0	5.88	9.96	8.1	84	44.9	150
	14:30	0.6	4.62	5.63	8.09	84	59.2	150
	16:30	0.6	5.05	6.4	8.1	84	62.1	150
15/9	10:00	0.2	6.36	7.84	7.79	80	69.7	175
	12:00	0.4	6.42	7	8.07	82	53.5	175
	14:00	0.6	5.05	5.55	8.13	86	6.7	175
	16:00	0.4	5.2	5.33	8.12	82		175
16/9	09:00	0.4	6.28	7.2	7.93	84		175
	10:30	0.4	5.36	6.63	8.05	80	53.5	175
	12:00	0	5.66	9.47	8.04	84	52.5	175
	13:30	0	4.48	4.95	8.16	86	54.5	175
	14:30	0.4	5.61	7.04	8.13	84	68.8	175
	16:30	0.4	5.39	6.68	7.94	86		175
17/9	10:00	0.2	5.37	6.55	7.94	84	60.2	175
	12:00	0.4	5.93	7.11	8.03	82	65.9	175
	14:00	0.6	18.77	14.73	8.09	86	68.8	175
20/9	09:00	0.4	5.79	9.62	7.47	80	50.6	175
	10:30	0.4	6.3	6.9	7.5	84	39.2	175
	12:00	0	5.45	5.48	7.52	80		175
	13:30	0	6.01	6.64	8.1	86	42.0	175
	14:30	0.6	5.33	6.48	8.11	84		175
	16:30	0.6	5.91	6.1	8.16	82		175
21/9	10:00	0.6	5.83	5.97	7.76	80	9.6	175
	12:00	0.6	4.98	5.28	7.77	78	42.0	175
	13:00	0.6	5.78	6.91	7.62	76	26.7	175

Table 5.3 : UV and UV/H_2O_2 oxidation

Day	UV Dosage (Ws/cm^2)	H_2O_2 Dosage (mg/ℓ)	Dissolved organic carbon (mg/ℓ)	Total organic carbon (mg/ℓ)	pH	Trihalomethane formation potential	Chlorophyll a (µg/ℓ)
15/9	100	0	7.76	8.96	7.52	116.9	9.6
		2	6.08	7.72	7.5	117.8	7.6
16/9		5	6.38	7.07	7.37	120.2	8.6
		10	6.54	7.18	7.31	108.6	3.8
17/9		15	7.36	8.88	7.21	146	15.3
		20	6.22	6.82	7.09	118	13.4
20/9	75	0	8.82	10.74	7.66	116.3	12.4
		5	14.83	12	7.48	112.1	10
22/9		20	7.53	7.9	7.15	87.2	
	20	0	6.41	6.55	7.86	131.7	21.5
		2	4.91	6.1	7.74	124.7	19.1
		5	4.77	5.59	7.71	84	17.2
23/9		10	14	15.96	7.61	89.3	21
		15	12.91	14.57	7.7	66.2	14.3
24/9		20	7.52	8.28	7.73	79.1	

Table 5.4 : Day trial one ($H_2O_2/O_3 = 0.6$)

22 SEPTEMBER (06:00)										
ID	Raw West	After O_3	After settling	After filtration	Raw East	After prechlorination	After settling	After filtration	Store East	Store West (O_3)
pH	7.41	7.38	8.92	8.52	7.45	7.38	8.96	8.49	8.5	8.42
NTU	79.2	77.9	4.3	0.49	81.6	81.9	4.4	0.59	0.32	0.33
Mn	0.03	0.05	0.01	0	0.02	0.05	0.01	0	0	0
Chl a	35.8	31.5	4.8	0	43	7.2	2.9	-0.5	0.5	0.5
TOC	6.59	7.57	6.06	4.23	10.2	6.23	5.63	5.21	7.13	6.78
THM									82.7	72.5
DOC	6.3	4.38	4.1	3.53	4.88	5.78	5.02	4.4	6.67	6.23
22 SEPTEMBER (08:00)										
pH	7.46	7.38	8.94	8.53	7.49	7.4	8.89	8.47	8.48	8.52
NTU	79.2	78.4	3.8	0.31	83.4	82.4	3.5	0.38	0.3	0.34
Mn	0.03	0.05	0.02	0.01	0.03	0.02	0.02	0.01	0	0.01
Chl a	55.9	34.4	3.8	1	41.6	12.9	4.8	0.5	1	0.5
TOC	7.04	6.48	4.68	5.75	7.63	8.65	4.85	4.24	4.48	5.12
THM									91.2	90.3
DOC	5.78	5.27	4.44	4.79	6.24	5.15	4.63	4.17	4.3	3.98
22 SEPTEMBER (10:00)										
pH	7.55	7.56	8.98	8.5	7.45	7.4	8.94	8.56	8.4	8.46
NTU	78.4	77.2	2.5	0.46	84.2	83.2	2.2	0.36	0.44	0.38
Mn	0.04	0.1	0.03	0.01	0.04	0.03	0.03	0.02	0.01	0.01
Chl a	41.6	37.3	1	1.4	41.6	8.6	2.9	-1.4	-1	-0.5
TOC	6.05	5.91	4.44	4.35	6.74	6.6	4.66	6.37	4.14	4.26
THM									86.1	62.9
DOC	3.91	4.06	3.98	3.29	4.44	4.92	4.25	3.68	3.97	3.99
22 SEPTEMBER (12:00)										
pH	7.5	7.49	8.94	8.59	7.63	7.38	8.96	8.6	8.58	8.6
NTU	83.7	80	2.5	0.4	82	82.4	2.5	0.42	0.39	0.4
Mn	0.06	0.1	0.01	0	0.06	0.03	0.02	0	0	0
Chl a	35.8	38.7	4.8	1.9	40.1	12.9	1.9	0.5	0	0
TOC	6.91	5.98	4.36	4.38	6.14	6.99	5.21	4.33	4.98	4.21
THM									95.5	88.2
DOC	3.93	4.93	3.91	4.06	4.6	4.32	3.46	4.06	3.9	4.03

APPENDIX 2

COST ANALYSES FOR OZONE GENERATION

Cost estimation for production of ozone - Refer to Chapter 6

COST ESTIMATION OF OZONE TREATMENT (From air)

Ozone output	M	30	kg/hr
Ozone dosage		1.3	mg/l
Specific energy consumption (18.3-19.	Es	19	kWh/kg O
Capital investment	Jo	9000000	R
Annual maintenance costs (5% of inves	U	450000	R/a
Cooling water consumption (2.92-4.17)	W	3.5	m3/kg O3
Electricity cost	X	0.15	R/kWh
Cost of cooling water	Y	0.5	R/m3
Construction period	b	1	a
Interest rate	i	11	% p.a.
Inflation	e	10	% p.a.
Depreciation period	n	10	a
Tax on investment	t	1	% p.a.
Investment related insurance	v	2	% p.a.
Annuity factor	ANF	0.192	
equivalent utilization period	EUP	8000	hr/a
Specific capital and fixed operational costs	SCC	84592	R h/kg a
Specific operational costs	SOC	36800	R h/kg a
Total annual costs	TAC	121392	R h/kg a
Cost of ozone generation		13.86	R/kg O3
Cost of water treated		1.801	cents/m3

COST ESTIMATION OF OZONE TREATMENT (From oxygen)

Ozone output	M	30	kg/hr
Ozone dosage		1.3	mg/l
Specific energy consumption (6.6-9.46)	Es	8	kWh/kg O
Capital investment	Jo	9000000	R
Annual maintenance costs	U	450000	R/a
Cooling water consumption (1.67-2.09)	W	1.9	m3/kg O3
Electricity cost	X	0.15	R/kWh
Cost of cooling water	Y	0.5	R/m3
Construction period	b	1	a
Interest rate	i	11	% p.a.
Inflation	e	10	% p.a.
Depreciation period	n	10	a
Tax on investment	t	1	% p.a.
Investment related insurance	v	2	% p.a.
Annuity factor	ANF	0.192	
equivalent utilization period	EUP	8000	hr/a
Specific oxygen consumption	Os	17	kg/kg O3
Cost of oxygen	Z	0.1	R/kg
Specific capital and fixed operational costs	SCC	84592	R h/kg a
Specific operational costs	SOC	30800	R h/kg a
Total annual costs	TAC	115392	R h/kg a
Cost of ozone generation		13.17	R/kg O3
Cost of water treated		1.712	cents/m3