Enhanced Coagulation for the Removal of Disinfection By-Product Precursors

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Executive Summary

Introduction

The discovery in the mid-seventies that disinfection of water can result in the formation of harmful disinfection by-products (DBP) through the reaction of the disinfectant with natural organic matter in the water resulted in the United States Environmental Protection Agency (USEPA) proposing the Disinfectants/Disinfection By-Products Rule in 1994. This rule sets maximum limits for residual disinfectant concentrations and maximum contaminant levels for disinfection by-products.

Coagulants have traditionally been used for turbidity removal, but coagulation is also able to bring about some removal of NOM. Since NOM generally acts as a DBP precursor, removal of NOM results in a lower DBP formation potential. The Disinfectants/Disinfection By-Products Rule requires that enhanced coagulation techniques be implemented, enhanced coagulation being defined as the addition of excess coagulant for improved removal of disinfectant by-products. When using enhanced coagulation techniques the coagulant dose that yields optimal NOM or DBP precursor removal is the most important factor, but effective turbidity removal must still be provided.

Although no regulations regarding NOM removal have been introduced into South Africa, the formation of DBP is still of great concern to those bodies which provide potable water. Conventional water treatment processes are not generally effective in removing DBP and their precursors and expensive treatment options, such as ozonation and granular activated carbon (GAC) are required for these applications. These processes are not suitable for use at small treatment works which lack the financial resources and skilled personnel required to operate them and enhanced coagulation could offer a viable alternative in such circumstances.

This project was undertaken to assess the effectiveness of enhanced coagulation for NOM and DBP removal and to compare it to the more advanced technologies of ozonation, advanced oxidation and GAC which were being investigated in another WRC project (WRC report K5/694/1 *The Treatment of Eutrophic Waters Using Pre- and Intermediate Ozonation, Peroxone and Granular Activated Carbon*).

Objectives

The objectives of this research programme were to:

- Assess the reduction in disinfection by-product precursors (DBP), pesticides/herbicides and taste and odour compounds (T&O) and natural organic matter (NOM) achievable using enhanced coagulation on water typical to Southern Africa.
- Assess the effect of coagulant type and dose, method of coagulant addition, pH, alkalinity, hardness, temperature and the nature of organic matter on the effectiveness of enhanced coagulation.
- Compare the removal of disinfection by-product precursors, pesticides/herbicides and taste and odour compounds obtained with enhanced coagulation with that achievable using ozonation and/or advanced oxidation with granular activated carbon (GAC) or bacteriologically activated carbon (BAC).
- Produce a report containing guidelines for enhanced coagulation for the treatment of different waters typical to Southern Africa.

Laboratory Tests

Laboratory tests were carried out on three different types of water:

1. A eutrophic water containing cyanobacteria (predominantly *Microcystis* or *Anabaena)* in cell concentrations varying between 10 000 and 500 000 cells/m*l*.
2. A clean water low in organic content.
3. A water high in organic contaminants from an industrial source.

Enhanced coagulation was carried out using alum, ferric chloride, a number of polymeric coagulants and magnetite (Sirofloc) at various concentrations in order to determine the coagulant dose required for optimal NOM removal as indicated by a number of surrogate NOM parameters. The effect of using organic polymeric coagulants, including a polyacrylamide, together with magnetite (Sirofloc) were also investigated.

The pH of the water was varied in order to determine the optimal pH for maximum TOC removal. In the case of the inorganic coagulants pH depression was carried out using coagulant alone, as well as with acid addition, while pH depression when using the polymeric coagulant obviously required acid addition.

The laboratory test work was carried out on jar test apparatus and all water samples were analysed for the following:

1) total and dissolved organic carbon
2) biodegradable dissolved organic carbon
3) turbidity
4) pH
5) alkalinity
6) geosmin and methylisoborneol
7) trihalomethane formation potential
8) UV absorbance (254 nm)
9) hardness
10) XAD-16 fractionation.

The combined effect of ozone followed by enhanced coagulation was also assessed. Since pre-ozonation requires equipment high in capital costs and highly skilled operators, an alternative, simpler method of pre-oxidation was also sought. Pre-chlorination was considered inappropriate as this would increase chlorinated DBP and therefore potassium permanganate was used. Pre-ozonation and pre-oxidation with permanganate prior to enhanced coagulation were carried out in order to directly compare both methods of pre-oxidation.

Pilot-plant Tests

A pilot-plant investigation was also carried out to confirm the findings of the laboratory tests. This was performed on the water treatment evaluation unit (WTEU) at Umgeni Water's Process Evaluation Facility (PEF). The WTEU is a flexible pilot water treatment plant with the capability to simulate a variety of conventional treatment systems. The unit consists of rapid mixing for coagulation, followed by pulsator clarifiers and rapid gravity filters. Enhanced coagulation using ferric chloride at concentrations varying between 6 and 30 mg/*l* were undertaken and the raw and final water obtained after enhanced coagulation treatment were analysed for a number of determinands, including THMFP, TOC, DOC, BDOC and UV absorption at 254 nm.

Summary of Results

The laboratory tests indicated that the inorganic coagulants such as ferric chloride and alum were generally better than the polymeric coagulants for removal of natural organic matter using enhanced coagulation. It was possible to obtain removals of up to 40% in trihalomethane formation potential (THMFP), up to 60% in total and dissolved organic carbon, between 70 and 90% in biodegradable dissolved organic carbon and between 70 and 90% in UV absorbance using ferric chloride and alum for enhanced coagulation. Enhanced coagulation was also very effective for colour reduction and removal of algal cells. These figures were confirmed by the pilot-scale tests.

The polymeric coagulants were less effective, generally resulting in not more than 10% reduction in organic carbon concentrations and having little or no effect on THMFP or biodegradable dissolved organic carbon. Decreases in UV absorbance of between 60 and 80% were possible using a polymeric coagulant.

Enhanced coagulation was not successful in removing micro-pollutants such as herbicides and taste and odour compounds.

Optimal NOM removal was found to occur at between 1,5 and 7 times the optimal coagulant concentration for turbidity removal, this being dependent on the concentration and nature of NOM in the water.

The pH was found to be important when using enhanced coagulation, with the optimal pH for removal of organic matter being around 5 when using ferric chloride and at between 5 and 5,5 when using alum. The pH was also found to affect NOM removal when using a polymeric coagulant, with the optimum pH being around 5. DOC removals using a polymeric coagulant could be increased by 15 to 25% by reducing the pH to around 5 using acid, without any adjustment to the coagulant dose.

Pre-oxidation of the water using ozone or permanganate prior to enhanced coagulation generally had little if any effect on the NOM removal possible using enhanced coagulation without pre-oxidation. However, it was possible to increase TOC and DOC removal by between 10 and 15% by pre-ozonating before enhanced coagulation treatment.

Magnetite does not appear to be a viable option for enhanced coagulation as it does not offer any significant benefits over other coagulants and would require very high concentrations.

Removals of NOM using enhanced coagulation were comparable or even better than those achieved with the more advanced treatment processes involving ozonation and granular activated carbon (GAC). However, for removal of micro-pollutants, ozone and or GAC would be required.

Guidelines for Enhanced Coagulation

The following guidelines were included for implementation of enhanced coagulation:

- Enhanced coagulation is effective for TOC, DOC, BDOC, THMFP and colour removal, but not for the removal of micro-pollutants and taste and odour compounds. This needs to be considered when deciding on the most appropriate treatment options for a particular situation.
- The inorganic coagulants such as ferric chloride and alum are generally more effective than the polymeric coagulants for enhanced coagulation applications.
- The optimal coagulant dose for enhanced coagulation effects is generally between 1,5 and 7 times the optimal coagulant dose for turbidity removal. These doses need to be assessed using laboratory, pilot-plant or full-scale tests.
- Alkalinity will adversely affect enhanced coagulation. Depressing the pH using acid to between 5 and 5,5 will increase the NOM removals achievable using enhanced coagulation.
- If determination of TOC or DOC is not possible, turbidity or UV absorbance (254 nm) can be used to determine optimal organic carbon removal.

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Enhanced Coagulation for the Removal of Disinfection By-Product Precursors

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1. Introduction

In the mid-seventies it was discovered that disaffection of water can result in the formation of harmful disaffection by-products (DBP) through the reaction of the disinfectant with natural organic matter (NOM) in the water (Symons *et al.*, 1975; Miltner *et al.*, 1992). In 1994 this resulted in the United States Environmental Protection Agency (USEPA) proposing the Disinfectants/Disinfection By-Products (D/DBP) Rule, which sets maximum limits for residual disinfectant concentrations and maximum contaminant levels for DBP (USEPA, 1994).

The conventional role of coagulation with metallic salts has been for turbidity removal, but coagulation is also able to bring about some removal of NOM. Since NOM generally acts as a DBP precursor, removal of NOM results in a lower DBP formation potential (Kavanaugh, 1978; Semmens and Field, 1980; Chadik and Amy, 1983; Reckhow and Singer, 1984; Hubel and Edzwald, 1987). When using enhanced coagulation techniques the coagulant dose that yields optimal NOM or DBP precursor removal is the most important factor, but effective turbidity removal must still be provided.

Although no regulations regarding NOM removal have been introduced into South Africa, the formation of DBP is still of great concern to those bodies which provide potable water. Conventional water treatment processes are not generally effective in removing DBP and their precursors and expensive treatment options, such as ozonation and granular activated carbon (GAC) are required for these applications. These processes are not suitable for use at small treatment works which lack the financial resources and skilled personnel required to operate them and enhanced coagulation could offer a viable alternative in such circumstances.

This project was undertaken to assess the effectiveness of enhanced coagulation for NOM and DBP removal and to compare it to the more advanced technologies of ozonation, advanced oxidation and GAC which were being investigated in another WRC project (WRC Report K5/694/1 *The Treatment of Eutrophic Waters Using Pre- and Intermediate Ozonation, Peroxone and Granular Activated Carbon*).

Objectives

The objectives of this research programme were to:

- Assess the reduction in disinfection by-product precursors (DBP), pesticides/herbicides and taste and odour compounds (T&O) and natural organic matter (NOM) achievable using enhanced coagulation on water typical to Southern Africa
- Assess the effect of coagulant type and dose, method of coagulant addition, pH, alkalinity, hardness, temperature and the nature of organic matter on the effectiveness of enhanced coagulation.
- Compare the removal of disinfection by-product precursors, pesticides/herbicides and taste and odour compounds obtained with enhanced coagulation with that achievable using ozonation and/or advanced oxidation with granular activated carbon (GAC) or bacteriologically activated carbon (BAC) (i.e. the results obtained from this project will be compared in terms of performance and cost-effectiveness with those obtained from the project on the treatment of eutrophic waters using pre- and intermediate ozonation, peroxone and granular activated carbon).
- Produce a report containing guidelines for enhanced coagulation for the treatment of different waters typical to Southern Africa.

2. Literature Review

Pollution of raw water supplies has resulted in the presence of herbicides, pesticides and other harmful organics as well as eutrophication and the subsequent taste and odour compounds produced by algal blooms. These organic compounds together with naturally occurring organic matter (NOM) have complicated water treatment, not only because they tend to pass through conventional treatment processes, but because they result in the formation of harmful by-products on disinfection of the water. Expensive treatment processes such as ozonation, advanced oxidation and granular activated carbon are gaining popularity, but these options are not always viable, especially at smaller water treatment facilities where both the capital costs and the need for skilled personnel to operate such processes preclude them.

The United States Environmental Protection Agency (USEPA) recently proposed requirements for the D/DBP Rule which will require many water treatment facilities in the United States to meet the requirements of enhanced coagulation (USEPA, 1994). Enhanced coagulation offers the possibility of significantly decreasing NOM present in the water without the need for costly upgrading of current treatment processes or the implementation of new technologies.

In general, conventional coagulation is defined by the conditions that lead to optimal turbidity removal using coagulant alone, while enhanced coagulation is defined by the conditions that lead to optimal NOM or DBP removal using a coagulant (usually inorganic e.g. alum or ferric chloride) with or without acid addition (Tryby *et al.*, 1993). Coagulation is an effective means of removing NOM from water and a number of researchers (Kavanaugh, 1978; Babcock and Singer, 1979; Glaser and Edzwald, 1979; Semmens and Field, 1980; Amy and Chadik, 1983; Dempsey *et al.*, 1984; Reckhow and Singer, 1984; Hubel and Edzwald, 1987; Hundt and O'Melia, 1988) have shown that precursor removals of up to 50 to 75% can be obtained using aluminium and ferric salts or by cationic polymers, depending on the nature of the organic matter. The impending USEPA D/DBP Rule, in addition to setting Maximum Contaminant Levels for THMs and haloacetic acids (HAA), establishes best available technologies for the reduction of natural organic matter.

Enhanced coagulation, which is defined in the proposed D/DBP Rule as the addition of excess coagulant for the improved removal of DBP precursors by conventional

filtration treatment (Crozes *et al.*, 1995), has been introduced as a requirement in the D/DBP Rule. The reasoning behind this move is that only a very small fraction of chlorination by-products and the associated health risks have been identified to date and therefore improved precursor removal would reduce both known and unknown risks from the water.

The D/DBP Rule has two steps (Crozes *et al.*, 1995); the first step sets TOC removal requirements based upon raw water TOC and alkalinity according to a 3 x 3 matrix (**Table 1)** (Crozes *et al.*, 1995). Obviously the higher the raw water TOC, the greater the percentage TOC removal achievable by enhanced coagulation. Quaism and co-workers (1992) in coagulation and softening tests conducted on natural waters, showed that TOC (and therefore NOM) removal is strongly pH dependent and Randtke (1988) found that the optimum pH range for NOM removal was 5,0 to 6,0. Therefore, the higher the alkalinity of the water, the lower the NOM removal that will be achievable using enhanced coagulation.

Table 1: Enhanced coagulation requirements of the D/DBP Rule for per cent TOC removal.

TOC	**Alkalinity mg/*l* as $CaCO_3$**		
mg/*l*	**<60**	**60-120**	**>120**
2-4	40%	30%	20%
4-8	45%	35%	25%
>8	50%	40%	30%

If a treatment utility is unable to meet the requirements of Step 1 of the D/DBP Rule, then Step 2 applies. This step was established to evaluate the "point of diminishing returns" for TOC removal (Crozes *et al.*, 1995). The point of diminishing returns is defined as a reduction of less than 0,3 mg/*l* residual TOC for each incremental addition of 10 mg/*l* or 5,5 mg/*l* alum or ferric chloride respectively. Incremental dosages of other coagulants can be determined on a molar basis using the metal (Al^{3+} or Fe^{3+}). Step 2 also requires that enhanced coagulation occurs at pH values less than or equal to a maximum value determined by the raw water alkalinity.

The impact of enhanced coagulation when used under Southern African conditions has not been assessed and it is possible that this treatment process may be adequate in many cases where more expensive treatment options have been considered.

Furthermore, not only the raw water TOC and alkalinity concentrations affect enhanced coagulation and these other factors need to be taken into consideration too when using enhanced coagulation. The coagulant type and dose are important, as is the nature of the organic matter (Singer and Harrington, 1993). In the case of inorganic coagulants it is possible to achieve the optimal pH values for maximum TOC removal using coagulant alone, although the addition of acid in conjunction with coagulant allows for a reduction in coagulant dose while still achieving the same TOC removals. With polymeric coagulants however, acid addition is required in order to obtain pH depression. Careful control of acid addition is required as poor floc formation and turbidity reduction can otherwise result (Tryby *et al.*, 1993).

Natural organic matter is usually divided into two major classes: hydrophobic and hydrophilic organic matter. The hydrophobic fraction is generally less soluble, of higher molecular size and contains greater aromaticity than the hydrophilic fraction (Singer and Harrington, 1993). The hydrophobic fraction consists basically of humic and fulvic acids, the humic acid fraction being highly reactive and readily removable by coagulation, while the fulvic acid fraction is less so (Randtke, 1988, Amy *et al.*, 1992). TOC is usually employed as a surrogate parameter for NOM, although trihalomethane formation potential and other DBP formation potential tests as well as UV extinction can also be used.

Enhanced coagulation may enable treatment facilities to significantly reduce DBP and other harmful organic contaminants at very little additional cost and may even obviate the need for much more costly and sophisticated treatment processes. Even if enhanced coagulation does not give rise to the required organic removal, used in conjunction with more expensive processes, it may be able to reduce the consumption of ozone and advanced oxidation chemicals and increase the lifetime of granular activated carbon beds.

3. Analytical Methodology

3.1 TOC, DOC, BDOC, AOC, THMFP, UV and NOM Fractionation

3.1.1 TOC, DOC and BDOC analysis

TOC and DOC concentrations were determined using the persulphate-ultraviolet oxidation method (method 5310C in *Standard Methods for the Examination of Water and Wastewater*, 1995) utilising an Aquadoc Total Organic Carbon Analyser. Prior to analysis of DOC, samples were filtered through 0,45 µm membrane filters (Millex, Millipore). All analyses were performed in at least duplicate.

Biodegradable dissolved organic carbon (BDOC) is defined as the fraction of DOC that is removed by heterotrophic microorganisms over a period of 28 days. Analyses were performed according to the method described by Servais *et al.* (1989). 200 m*l* of sample was sterilised by filtration through 0,2 µm membrane filters (Sartorius cellulose acetate membrane filters), carefully rinsed first with ultrapure water (Millipore Milli-Q) and then with water sample. An inoculum was prepared by filtering water obtained from the same environment as the sample through a 1,2 µm membrane filter (Sartorius cellulose acetate membrane filter). The method described by Servais *et al.* (1989) called for a 2,0 µm filter for filtration of the inoculum, but despite repeated efforts to obtain these filters, it became necessary to use the 1,2 µm filters instead. 200 m*l* of sterilised sample was inoculated with 2 m*l* of inoculum before being poured into a 100 m*l* glass stoppered reagent bottle, which was completely filled with sample and water sealed. The sample was incubated in the dark at between 20 and 22°C for 28 days. Analysis of the DOC was carried out on a subsample of the water collected prior to incubation and on the sample at the end of the incubation period. In this case filtration was obviously through a 0,2 µm membrane filter and not a 0,45 µm membrane filter as described above for DOC analysis The BDOC value was calculated as the difference between the initial and final DOC results.

3.1.2 AOC Analysis

The method used for assimilable organic carbon analysis was based on that proposed in *Standard Methods* (1995) with slight modifications introduced from the procedure proposed by Van der Kooij *et al.* (1982). The samples were inoculated with between

50 and 500 CFU/m*l* each of P17 and NOX stock cultures and incubated in the dark at between 15 and 25°C for a period of approximately 3 weeks until maximum density growth had occurred. Enumeration of the test bacteria during the incubation period was carried out as described in *Standard Methods* (1995). Calculation of the AOC was carried out using the equation proposed by Van der Kooij *et al.* (1982).

3.1.3 THMFP Analysis

THMFP was determined using the THMFP test described in section 5710B of *Standard Methods* (1995), although the test was carried out at a pH of 9,2 ± 0,2 as recommended in section 5710C of the 18th Edition of *Standard Methods* (1992) for the basic THMFP test. This test simulates the conditions experienced in high pH waters and accelerates THM formation. A measured amount of the water sample was placed in a glass stoppered bottle and sufficient chlorine was added to the water sample to ensure that a chlorine residual of at least 3 mg/*l*, but not more than 5 mg/*l* remained at the end of the 7 day incubation period. The pH of the chlorinated water sample was raised to 9,2 ± 0,2 and the bottle was water sealed and incubated in the dark at 25 ± 2°C for 7 days. The THM concentration of the water sample prior to chlorination and at the end of the 7 day incubation period was measured and the THMFP calculated from the difference between these THM concentrations.

THMs were determined on a Varian 3600 gas chromatograph using direct aqueous injection with a suitable thermal programme and an internal 1,2-dibromomethane standard.

3.1.4 UV absorbance

UV absorbance of water samples, after filtration through 0,45 µm membrane filters (Millex, Millipore), was measured at 254 nm using a Pharmacia Ultraspec III spectrophotometer and Autofill III autosampler with a 10 mm quartz cell. The UV light source was provided by a deuterium lamp. The procedure followed is described in section 5910B of *Standard Methods* (1995).

3.1.5 Fractionation of NOM

Fractionation of the NOM present in both treated and untreated water samples was carried out using an Amberlite XAD-16 resin (Rohm and Haas, Philadelphia, PA) according to the procedure described by Thurman and Malcolm (1981). The fractionated effluents and the original sample were analysed for DOC on an Aquadoc Total Organic Carbon Analyser as described in **Section 3.1.1**.

3.2 Micropollutants: Geosmin, 2-MIB and Atrazine

One litre of the sample was extracted with three 50 m*l* portions of dichloromethane and then concentrated under vacuum on a rotary evaporator to produce a final concentrate solution of 1 m*l*. The geosmin, 2-MIB and atrazine concentrations were determined on a Hewlett-Packard 5890/5970 gas chromatograph-mass selective detector according to an NLA accredited procedure for geosmin and 2-MIB and an Umgeni Water method for atrazine.

3.3 Algal Identification and Enumeration

Algal identification and enumeration was carried out by the Hydrobiology section of the Scientific Services Division of Umgeni Water using an NLA accredited procedure.

3.4 Chemical Analyses

3.4.1 pH

pH was measured on a Radiometer PHM 95 pH/ion meter.

3.4.2 Turbidity

Turbidity was determined using a Hach Ratio/XR model 43900 turbidity meter.

3.4.3 Colour

Samples were filtered through a 0,45 µm membrane filter (Millex, Millipore) prior to colour measurement. Colour was determined relative to a chloroplatinate standard at 400 nm on a Shimadzu UV 2100 spectrophotometer according to an NLA accredited procedure.

3.4.4 Calcium, magnesium and hardness

Calcium and magnesium were determined using ICP-AES on a Varian Radial ICP according to an NLA accredited method. Hardness was calculated from the calcium and magnesium analyses.

3.4.5 Iron

Iron was analysed by ICP-AES on a Varian Radial ICP according to an NLA accredited method.

3.4.6 Manganese

Manganese was analysed by ICP-AES on a Varian Radial ICP according to an NLA accredited method.

3.4.7 Alkalinity

Alkalinity analyses were performed on a Mettler DL25 Autotitrator using 0,02 N HCl and titrating to pH 8,2 and 4,3 according to an NLA accredited method.

3.5 Determination of Ozone

3.5.1 Iodometric titration for the determination of ozone

An iodometric titration method was used for measuring ozone concentration in the reactor column during calibration or for determination of the ozone concentration in the off-gas from the reactor column. The method involves the liberation of iodine from potassium iodide by ozone, followed by titration of the liberated iodine with sodium thiosulphate. The titration was carried out at a pH of between 3 and 4 since the reaction is not stoichiometric at neutral pH as a result of partial oxidation of the thiosulphate to sulphate. This method is suitable for measuring concentrations of ozone of around 1 mg/*l* or higher, but is subject to interference from strong oxidising agents, such as chlorine and hydrogen peroxide.

The method used is described in section 4500-Cl B of *Standard Methods* (1995). It was not necessary to add KI to the sample prior to titration since this procedure was only used in cases where ozone was passed through KI solutions, as was the case during calibration of the ozone apparatus or for the KI trap used to measure the ozone concentration in the off-gas from the ozone reactor column. A measured volume of

the KI-iodine solution was placed in a flask together with 5 ml glacial acetic acid and titrated against 0,01 N sodium thiosulphate until the yellow colour of the liberated iodine had almost disappeared. 1 m*l* of starch was then added and titration continued until the blue colour had completely disappeared.

3.5.2 Indigo colorimetric method for the determination of ozone

The indigo colorimetric method was used for measurement of dissolved ozone in water samples. This method is based on the principle that under acidic conditions, ozone rapidly decolorises indigo dye and the decrease in absorption is linearly proportional to the ozone concentration. The method used is described in section 4500-O3 B of *Standard Methods* (1995). 10 m*l* of indigo reagent were placed in a 100 ml volumetric flask and the flask was filled to the mark with the ozone-containing sample or a dilution of the sample, ensuring that complete decoloration of the indigo did not occur. A sample blank was prepared using ozonated sample from which the ozone was first removed by the addition of sodium thiosulphate. This solution was then used to fill a 100 m*l* volumetric flask containing 10 m*l* indigo reagent to the mark. The absorbance of the samples and sample blank were measured at 600 nm on a Pharmacia Ultraspec III spectrophotometer and Autofill III autosampler using a 10 mm quartz cell. The ozone concentration in a sample was calculated from the difference between the blank and sample absorbance.

4. Experimental Procedures

According to the original project plan as laid down in the project submission form, enhanced coagulation was carried out on three different types of water which corresponded with those being used in the WRC project on *The Treatment of Eutrophic Waters using Pre- and Intermediate Ozonation, Peroxone and Pica Carbon* (WRC Report K5/694/1). These were namely:

1. A eutrophic water containing cyanobacteria (predominantly *Microcystis* or *Anabaena)* in cell concentrations varying between 10 000 and 500 000 cells/m*l*.
2. A clean water low in organic content.
3. A water high in organic contaminants from an industrial source.

Enhanced coagulation was carried out using alum, ferric chloride, a number of polymeric coagulants and magnetite (Sirofloc) at various concentrations in order to determine the coagulant dose required for optimal NOM removal as indicated by a number of surrogate NOM parameters. The effect of using organic polymeric coagulants, including a polyacrylamide, together with magnetite (Sirofloc) was also investigated.

The pH of the water was varied in order to determine the optimal pH for maximum TOC removal. In the case of the inorganic coagulants pH depression was carried out using coagulant alone, as well as with acid addition, while pH depression when using the polymeric coagulant obviously required acid addition.

The laboratory test work was carried out on jar test apparatus and all water samples were analysed for the following:

1) total and dissolved organic carbon (TOC and DOC)
2) biodegradable dissolved organic carbon (BDOC)
3) turbidity
4) pH
5) alkalinity
6) geosmin and methylisoborneol
7) trihalomethane formation potential (THMFP)
8) UV absorbance (254 nm)
9) hardness

10) XAD-16 fractionation.

The combined effect of ozone followed by enhanced coagulation was also assessed. Since pre-ozonation requires equipment high in capital costs and highly skilled operators, an alternative, simpler method of pre-oxidation was also sought. Pre-chlorination was considered inappropriate as this would increase chlorinated DBP and therefore potassium permanganate was used. Pre-ozonation and pre-oxidation with permanganate prior to enhanced coagulation were carried out in order to directly compare both methods of pre-oxidation.

4.1 Preparation of Water Samples

4.1.1 Source of water samples

Three types of water were used in this investigation, these being:

1. A eutrophic water containing cyanobacteria (predominantly *Microcystis* or *Anabaena)* in cell concentrations varying between 10 000 and 500 000 cells/m*l*.
2. A clean water low in organic content.
3. A water high in organic contaminants from an industrial source.

Since a constant source of eutrophic water was not available during the period that this investigation was carried out, eutrophic samples were produced by spiking Inanda Dam water with cyanobacterial scums containing predominantly either *Microcystis* or *Anabaena* to produce water with varying algal cell concentrations. Inanda Dam water without any algal cell addition was used for the second water type, while water from the Sterkspruit River, a stream which runs through the industrial area of Hammarsdale and which is contaminated with industrial effluents was used for the third water type.

The industrially polluted water was spiked with atrazine and the eutrophic water was spiked with geosmin, 2-methyliosborneol (2-MIB) and atrazine.

4.1.2 Algal cell collection and spiking

A number of difficulties were experienced in obtaining algal cell cultures of predominantly *Microcystis* or *Anabaena* cyanobacteria. As it was not possible to find eutrophic water of a consistent source it became necessary to obtain algal cultures from any available source. Cultures containing predominantly *Microcystis* were

obtained from Inanda, Nagle and Hazelmere Dams. Predominantly *Anabaena*-containing cultures were obtained from Inanda and Albert Falls Dams and pure cultures of *Anabaena* were also grown in the Hydrobiology laboratories of Umgeni Water and used for this project.

The algal scum samples were identified and enumerated as described in **Section 3.3**. The amount of algal scum that needed to be added to a measured volume of water to yield a final cell count of 10 000 and 100 000 *Microcystis* or *Anabaena* cells/m*l* was then calculated from the algal cell count. It was not possible to spike the water at cell concentrations of higher than 100 000 cells/m*l* due to both limited supplies and the relatively low cell concentrations of the cyanobacterial samples.

In general 22 *l* of water sample was measured into a 25 *l* capacity bucket. The algal scum was mixed well and the required amount was measured and added to the water. The water was well mixed prior to sample extraction to ensure even dispersion of the algal cells. Algal cell counts were carried out on the algal spiked water both before and after any treatment had been performed on it.

4.2 Preparation of Coagulants

Ferric chloride, alum, a number of polymeric coagulants and magnetite (Sirofloc), both on its own and together with polymeric coagulants, including polyacrylamide were used for coagulation.

The ferric chloride, which was supplied as approximately 43% $FeCl_3$, was diluted to 0,08% as $FeCl_3$, so that 1 m*l* solution yielded 1 mg/*l* $FeCl_3$ when added to 800 m*l* sample. The alum was provided as a 46 to 48% m/v solution. The concentration of the solution was determined by measuring the specific gravity of the solution and then based on this a 0,16% alum solution as $Al_2(SO_4)_3.14H_2O$ was prepared. 1 m*l* of this solution when added to 800 m*l* sample was equivalent to 2 mg/*l* as $Al_2(SO_4)_3.14H_2O$.

The polymeric coagulants used were a blended polyaluminium chloride (PACl) and dimethyldiallylammonium chloride (DMDAAC) (Z464N, Zetachem), unblended polyamines (PA) (C577 and U5000, NCP-Ultrafloc), a blended PACl and PA (Primco 735, LPM) and an unblended DMDAAC (Catfloc S, Floccotan).The polymeric coagulants were diluted to 0,08% solutions so that 1 m*l* of coagulant

solution corresponded to a coagulant dose of 1 mg/*l* when added to an 800 m*l* subsample of water.

Magnetite (Sirofloc) was obtained from Kaverner Davy (Pty) Ltd and was prepared according to the manufacturer's instructions. A pre-weighed amount (200 g) of dry Sirofloc was thoroughly washed with RO water (Millipore). The water was decanted and 2 *l* of sodium hydroxide (0,1 N) was then added to the slurry of magnetite which was stirred for ten minutes and then allowed to settle. The liquid was decanted and the magnetite was washed three times with 2 *l* portions of RO water (Millipore), with stirring for five minutes followed by settling for each washing. The liquid was decanted and the magnetite slurry was then made up as a 250 m*l* solution (i.e. 80%). Suitable dilutions of this stock solution were used for dosing. Magnetite concentrations of between 250 and 60 000 mg/*l* were used. Tests were carried out in which magnetite was used as the only coagulant as well as tests where it was used in conjunction with polymeric coagulants. The polymeric coagulants were used at concentrations of between 1 and 40 mg/*l* together with magnetite at the dose giving optimal DOC removal. The polyacrylamide (LT22, Chemserve Colloids) however was used at concentrations of 0,2 and 2,5 mg/*l*. The coagulants used in conjunction with magnetite were a blended PACl and DMDAAC (Z464N, Zetachem) and a PA (U5000, NCP-Ultrafloc).

4.3 Standard Jar Test (Coagulation Test)

A standard jar test procedure (Hudson and Wagner, 1981) was used to simulate the conventional treatment processes of coagulation, flocculation and settling. Jar tests were carried out on an Aztec or a Phipps and Bird 6 paddle jar stirrer apparatus with varying speed control. 800 m*l* subsamples of the water were placed in 1 *l* capacity cylindrical glass beakers and stirred at 300 r/min (this corresponds to a G value of between 200 and 300 s^{-1}). The coagulant was added and stirring at 300 r/min was continued for 2 minutes after the addition of coagulant, after which the stirring speed was reduced to 40 r/min. Stirring at 40 r/min continued for another 15 minutes. The floc size and settling rate were noted and the water was allowed to settle for 15 minutes before being filtered through Whatman number 1 equivalent filter paper (M&N Rundfilter).

A range of coagulant concentrations was utilised in order to determine both the optimum dose for turbidity removal as well as the optimum dose for maximum DOC removal. The optimum dose for turbidity removal was taken as the minimum

coagulant concentration which would produce a final filtered water turbidity of less than 0,5 NTU.

4.4 Ozonation Procedure

Laboratory ozonation was carried out in one of two glass contact columns. The smaller column was 1,40 m high with an internal diameter of 6 cm and a capacity of 4 *l*, while the larger column, which had a capacity of a little over 10 *l*, was 1,57 m high with an internal diameter of approximately 9 cm. A Sorbios laboratory ozone generator model GSG 1.2 capable of producing 1 g ozone per hour was used to generate ozone from oxygen (>99.5% oxygen, < 10 mg/*l* moisture) at a pressure of 0,5 bar and a flow rate of 15 *l*/h. The apparatus consisted of glass, stainless steel and Teflon with silicon tubing.

The ozone was introduced into the column through a sintered glass diffuser (No. 1 diffuser) positioned at the base of the column. Gas exiting the column was fed through a KI trap before passing through a gas flow meter (Alexander Wright Model Number DM3 B). The contact column was calibrated by filling it with a solution of KI and passing a measured volume of ozone-containing gas through the column. During ozonation the solution was recirculated from the bottom of the contact column to the top using a peristaltic pump. Ozone liberates iodine from KI and the amount of liberated iodine after ozonation was measured using an iodometric titration as described in **Section 3.5.1**. The process was repeated until at least three calibrations varying not more than 5% in concentration had been obtained. It was then possible to calculate the amount of ozone-containing gas that would have to be added to the sample for a particular applied ozone dose.

When ozonating a water sample, a measured volume of the water was placed in the column after calibration had been completed, the water was recirculated to prevent the formation of concentration gradients and the required amount of ozone-containing gas was passed through the contact column. Recirculation of the sample continued for a period of four minutes after onset of ozonation regardless of the how long it took to add the ozone-containing gas (it never took more than four minutes to add the ozone). Thereafter the ozone residual in the water was determined using the indigo trisulphonate method as described in **Section 3.5.2**. The ozone residual was measured at the end of the four minute recirculation period and thereafter at four minute intervals for a period of up to sixteen minutes after the four minute recirculation

period had ended. The initial ozone residual recorded at 0 minutes was therefore taken at termination of the four minute recirculation and contact period. The amount of unreacted ozone exiting the column in the gas phase was also determined by measuring the amount of liberated ozone in the potassium iodide trap at the exit from the column using an iodometric titration (**Section 3.5.1**).

4.5 Pre-oxidation with Permanganate

Potassium permanganate ($KMNO_4$) was prepared as a 0,05 M solution in ultrapure water (Millipore Milli-Q). Serial dilutions of the stock solution were used for dosing. Permanganate was used in two concentration ranges, the first being 0,025 to 0,10 mg $KMNO_4$/mg DOC and the second 0,10 to 0,40 mg $KMNO_4$/mg DOC. The permanganate was added directly prior to the coagulant while stirring at 300 r/min on a jar stirrer apparatus. The jar test then proceeded as described in **Section 4.2.3**. Pre-ozonation was carried out in parallel with the permanganate tests using the same concentration ranges (i.e. 0,025 to 0,10 mg O_3/mg DOC and 0,10 to 0,40 mg O_3/mg DOC) and using the procedure described in **Section 4.2.4**.

4.6 Fractionation of NOM

Adsorption chromatography using an Amberlite XAD-16 resin (Rohm and Haas, Philadelphia, PA) was employed to fractionate the dissolved organic matter present in both the untreated and treated water samples into hydrophobic and hydrophilic fractions. The Amberlite resin was prepared according to the procedure described by Thurman and Malcolm (1981), involving rinsing in sodium hydroxide (0,1N) followed by sequential extraction in a Soxhlet using methanol, diethyl ether, acetonitrile and methanol. The fractionation procedure followed was also that described by Thurman and Malcolm (1981). Sample aliquots of either 1,0 *l* or 0,5 *l* were acidified to pH 2 using hydrochloric acid (0,1 N) and then applied to a 2 cm diameter column of resin (approximately 8 m*l* resin) and eluted with hydrochloric acid (0,1 N) at a flow rate of 2,5 m*l*/min. The acidic effluent collected off the column contained the hydrophilic fraction. The resin was then eluted with sodium hydroxide (0,1 N), the eluent containing the hydrophobic fraction. Both the acidic effluent and the basic eluent were pH corrected to the ambient pH of the original sample. The DOC of the original sample and the pH-corrected fractionated samples were measured on an Aquadoc Total Organic Carbon Analyser as described in **Section 3.1.1**.

4.7 Pilot-plant Investigation

The pilot-plant investigation was carried out on the water treatment evaluation unit (WTEU) at Umgeni Water's Process Evaluation Facility (PEF). The WTEU is a pilot-scale water treatment unit providing facilities for conventional water treatment processes. Enhanced coagulation using ferric chloride at concentrations varying between 6 and 30 mg/*l* were undertaken in order to confirm the findings of the laboratory tests. The raw and final water obtained after enhanced coagulation treatment were analysed for a number of determinands, including THMFP, TOC, DOC, BDOC and UV absorption at 254 nm.

The WTEU was designed as a flexible pilot water treatment plant with the capability to simulate a variety of conventional treatment systems. The unit consists of rapid mixing for coagulation, followed by pulsator clarifiers and rapid gravity filters.

5. Results and Discussion

5.1 Effect of Enhanced Coagulation on NOM

5.1.1 Disinfection by-product precursors

Enhanced coagulation was often found to have little or no effect on the THMFP. However, in higher DOC waters, such as eutrophic waters, THMFP removals of around 50% were possible using ferric chloride for enhanced coagulation at concentrations of 1,5 to 5 times the optimum turbidity removal dose **Figure 1**. This was confirmed by pilot-scale studies in which THMFP removals of up to 40% were obtained when using ferric chloride for enhanced coagulation of Inanda Dam raw water at concentrations of between 6 and 30 mg/*l* (i.e. 2 to 5 times the optimum dose for turbidity removal) (**Figure 2)**.

Removals of between 50 and 75% of DBP have been cited in the literature (Amy and Chadik, 1983; Babcock and Singer, 1979; Dempsey *et al.*, 1984; Glaser and Edzwald, 1979; Hubel and Edzwald, 1987; Hundt and O'Melia, 1988; Kavanaugh, 1978; Reckhow and Singer, 1984; Semmens and Field, 1980), although this does depend on the nature of the organic matter present in the water.

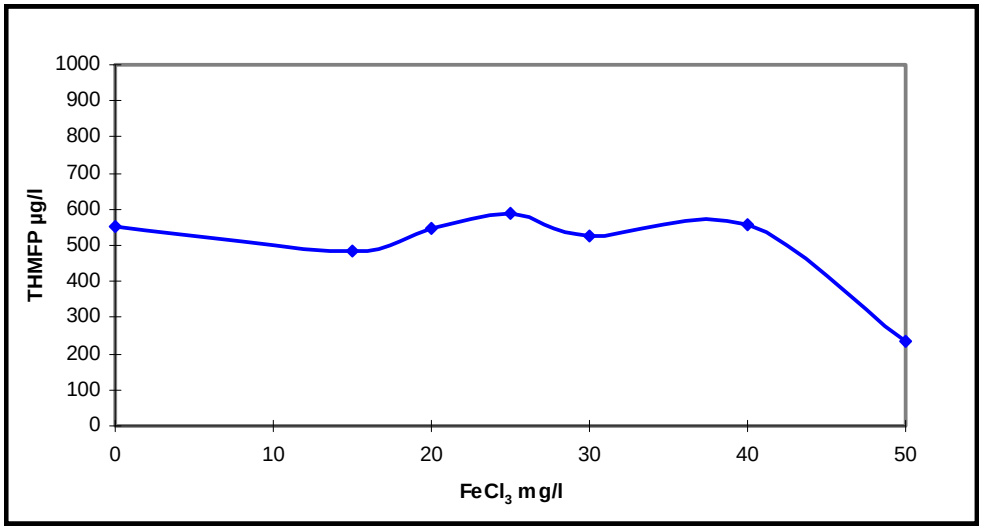

Figure 1: Effect of enhanced coagulation on the THMFP of a eutrophic water (Inanda Dam water with 100 000 *Microcystis* cells/m*l*).

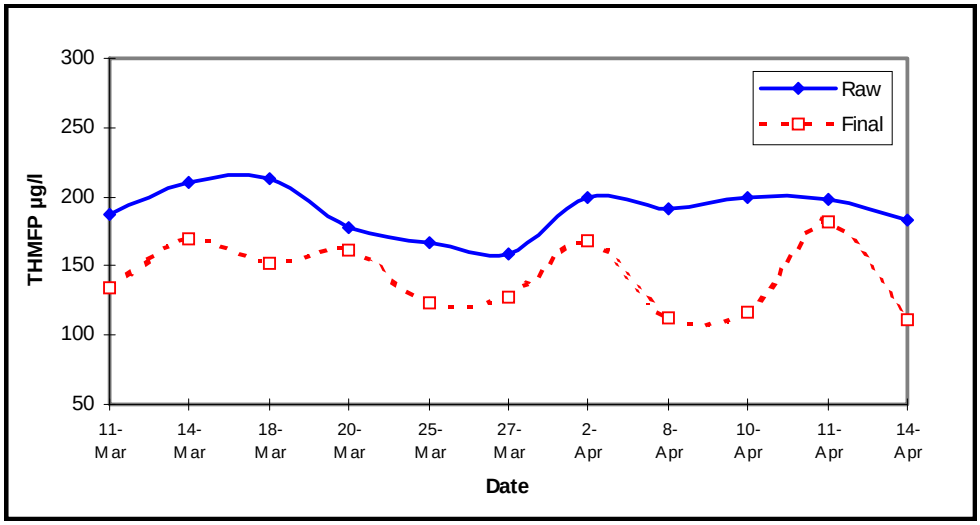

Figure 2: Pilot-scale results depicting effect of enhanced coagulation on THMFP.

5.1.2 Total and dissolved organic carbon (TOC and DOC)

Enhanced coagulation of Inanda Dam raw water, both with and without algal addition to simulate eutrophic conditions, generally yielded TOC and DOC removals of between 20 and 40% and even up to 50% when using the inorganic coagulants (ferric chloride and alum) (**Figure 3)**. These removals were obtained at inorganic coagulant doses in the region of 1,5 to 5 times the concentration required for optimal turbidity removal. The organic polymeric coagulants did not bring about more than approximately 10% TOC and DOC removal, even in waters containing algal cells at concentrations of up 100 000 cells/m*l* when using coagulant concentrations 6 times the optimal dose for turbidity removal.

It should be noted that the TOC of these waters consisted predominantly of DOC. It was therefore not surprising to find that the effect of enhanced coagulation on the DOC content of the water mirrored that for the TOC content (**Figure 3)**. The TOC and DOC concentrations of these waters was generally between 4 and 8 mg/*l*.

The pilot scale tests carried out on Inanda Dam raw water using ferric chloride confirmed the results of the laboratory tests. At ferric chloride concentrations of approximately 8 to 18 mg/*l* (i.e. 2 to 3 times the optimum turbidity removal dose) TOC and DOC removals in the region of 20 to 40% were obtained. Increasing the dose to 30 mg/*l* $FeCl_3$ (approximately 5 times the optimum turbidity removal dose), it was possible to achieve between 50 and 75% removal of TOC and DOC. **Figure 4**

graphically presents TOC data from the pilot-plant investigation (from 11 March to 10 April and from 24 April to 29 April ferric chloride doses of between 8 and 18 mg/*l* were used, while doses of 30 mg/*l* were used between 14 April and 18 April).

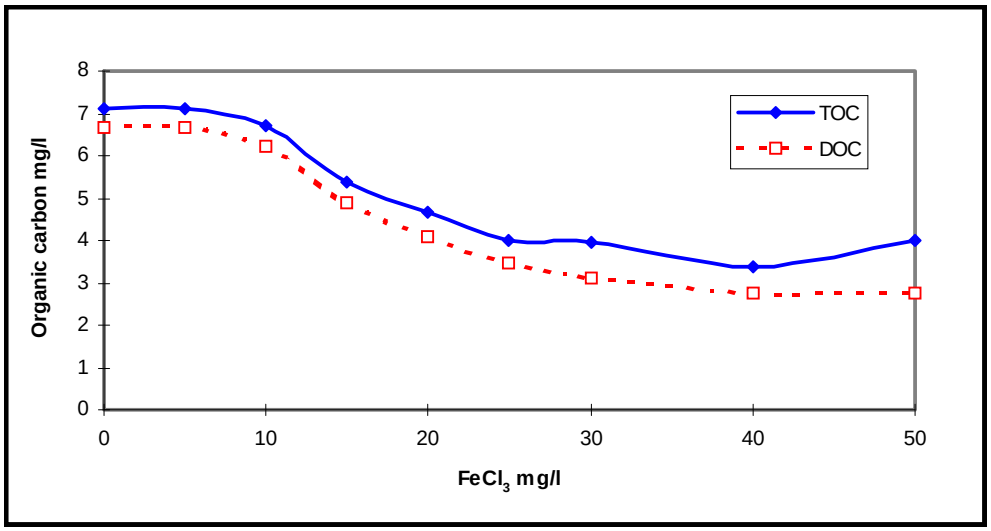

Figure 3: **Effect of enhanced coagulation on the TOC and DOC of a eutrophic water (Inanda Dam water containing 10 000 *Anabaena* cells/m*l*).**

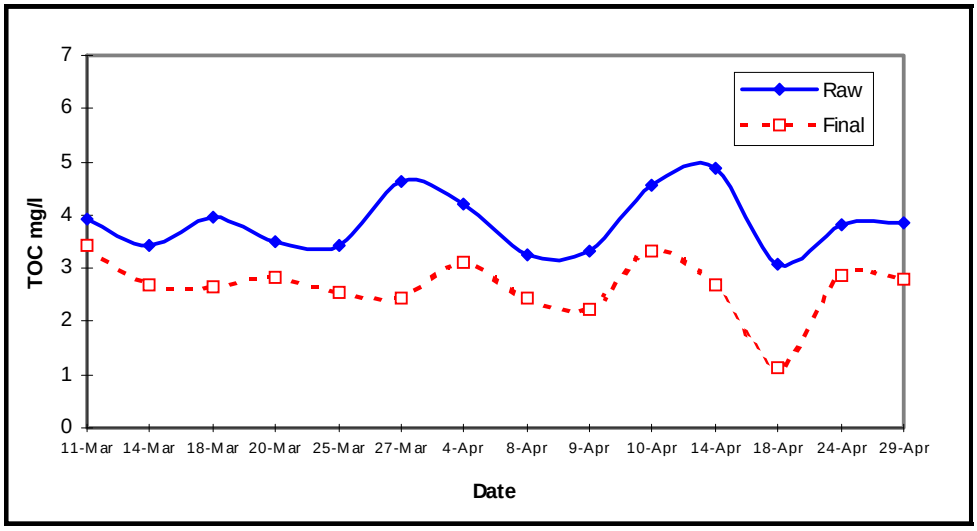

Figure 4: **Pilot-plant results depicting the effect of enhanced coagulation on TOC.**

Better TOC and DOC removals were obtained for enhanced coagulation of an industrially polluted water. The TOC and DOC of the industrially polluted water was found to be fairly variable, falling between 15 and 35 mg/*l*. It was possible to achieve TOC and DOC removals of 60% and more from these water samples when using ferric chloride and alum (**Figure 5)**. The optimal coagulant dose for organic carbon

removal was anywhere between 1,5 and 7 times the optimal dose for turbidity removal.

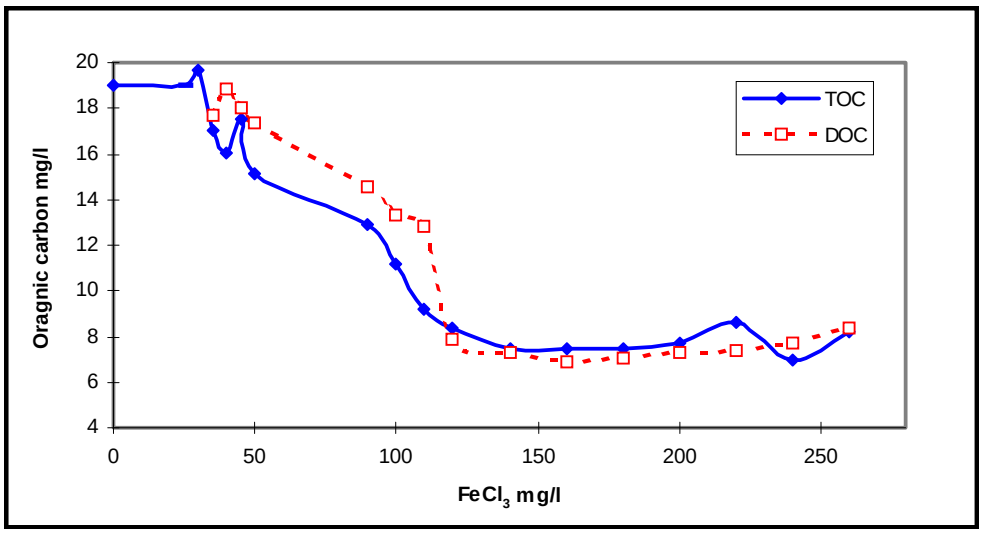

Figure 5: Effect of enhanced coagulation on the TOC and DOC of an industrially polluted water.

It was also possible to achieve TOC and DOC removals of around 50% from the industrially polluted water when using an organic polymeric coagulant. However, it must be noted that this coagulant was not generally suitable for the treatment of this water in terms of turbidity removal and in most cases it was not possible to produce water of acceptable quality, even at concentrations as high as 70 mg/*l* . Doses as high as this would not be economical especially in light of the fact that ferric chloride and alum are effective for organic carbon removal and also achieve acceptable final water quality.

In the case of the industrially polluted water the TOC was again found to consist predominantly of DOC and therefore enhanced coagulation had much the same effect on both TOC and DOC (**Figure 5)**.

5.1.3 Biodegradable dissolved organic carbon (BDOC) and assimilable organic carbon (AOC)

BDOC removals were in many cases fairly good (30 to 50%) at the ferric chloride and alum doses which gave optimal turbidity removal and it was possible to obtain between 70 and 90% removal when using between 2 and 5 times the optimal turbidity removal dose (**Figure 6)**. Ferric chloride generally gave better BDOC removals than did alum, while the organic polymers resulted in little or no reduction in BDOC.

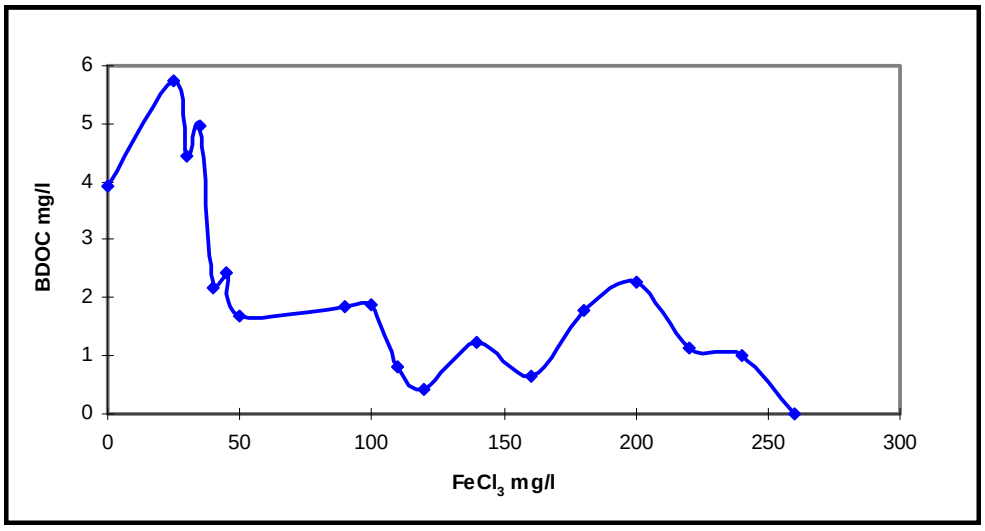

Figure 6: Effect of enhanced coagulation ($FeCl_3$) on the BDOC of an industrially polluted water.

The biodegradable dissolved organic matter which is present in a water can be determined using either the BDOC or assimilable organic carbon (AOC) tests. However, these two tests are essentially different, the BDOC being the portion of DOC that can be mineralised by heterotrophic micro-organisms, while AOC is the portion of DOC that can be converted to biomass (Huck, 1990a). BDOC is determined by measuring the decrease in DOC that occurs in an inoculated water over a given period of time, so that in other words BDOC corresponds to the difference between initial DOC and that reached after the given period of time (Frias *et al.*, 1992; Lucena *et al.*, 1990; Servais *et al.*, 1987, 1989). In contrast AOC is determined by measuring the biomass formed as a result of biodegradable carbon assimilation (Huck, 1990) and this can be done by means of heterotrophic plate count according to the procedure described by Van der Kooij and co-workers (1982), or using other methods such as measurement of the concentration of intracellular ATP (adenosine triphosphate) or the increase in turbidity (Frias *et al.*, 1995).

Some AOC tests were carried out in this investigation in order that the BDOC and AOC tests could be compared, although it was only possible to perform AOC tests on a few samples. The AOC results, although measured in quite different units from the BDOC test, correlated well with the BDOC results indicating similar trends.

5.1.4 UV absorbance at 254 nm

The UV absorbance was found to correlate strongly with both the turbidity and the TOC/DOC (**Figure 7)**. In low DOC waters (<7 mg/*l*), almost complete UV extinction at 254 nm was obtained at the optimal inorganic coagulant doses for turbidity removal. The organic polymeric coagulants were not as effective in reducing UV absorption, but were able to reduce the UV by as much as 60 to 80%. However, polymeric coagulant doses higher than the optimum for turbidity removal, generally gave little or no additional UV removal.

Reductions in UV absorbance in eutrophic waters and industrially polluted water, which were higher in TOC (generally between 7 and 35 mg/*l*), were usually between 50 and 75% at the optimal alum and ferric chloride doses for turbidity removal. Using between 2 and 4 times these concentrations could increase UV removals to between 70 and 90%.

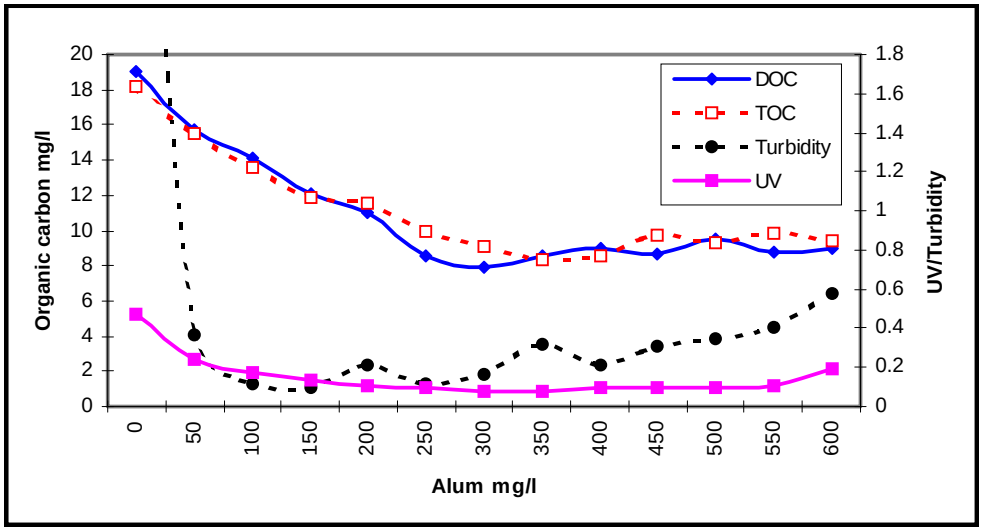

Figure 7: Effect of enhanced coagulation on the UV (254 nm), TOC, DOC and turbidity of an industrially polluted water.

The organic polymeric coagulants could bring about UV removals of as much as 80% at the optimum turbidity removal concentrations and using in the region of double the turbidity removal doses, UV removals of up to 90% were possible. However, the polymeric coagulants were not always suitable in terms of turbidity removal for the treatment of the industrially polluted water. In spite of this it was possible to get between 50 and 60% reduction in UV absorbance using an organic polymer even when the turbidity of the treated water was unacceptable. In such cases, the organic polymers would not be suitable for enhanced coagulation processes.

The results of the pilot-plant investigation confirmed the laboratory results, indicating that UV removals in the region of 50 to 75% could be obtained at ferric chloride concentrations of between 8 and 18 mg/*l* (i.e. 2 to 3 times the optimal turbidity removal dose). UV removals of between 80 and 90% were obtained when the ferric chloride dose was increased to around 30 mg/*l* (approximately 5 times that for optimal turbidity removal). See **Figure 8** in which ferric chloride doses of between 8 and 18 mg/*l* were used from 11 March to 10 April and from 24 April to 29 April, while doses of 30 mg/*l* were used between 14 April and 18 April.

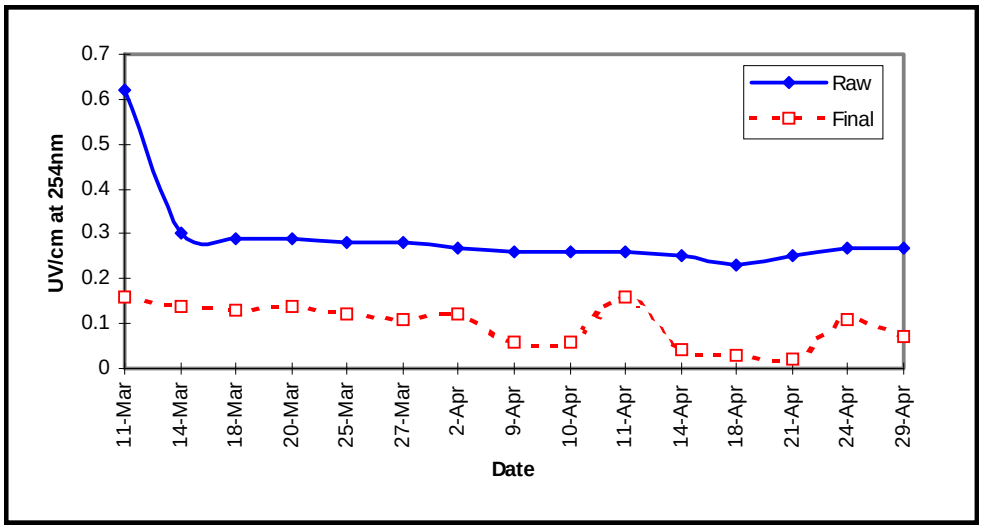

Figure 8: Pilot-plant results depicting the effect of enhanced coagulation on the UV absorbance at 254 nm.

5.1.5 Micro-pollutants

Enhanced coagulation using ferric chloride, alum or a polymeric coagulant did not generally give rise to any significant removal of geosmin, MIB or atrazine. However, in some cases enhanced coagulation with either ferric chloride or alum did bring about as much as 50% removal of geosmin, but the general trend was for little or no removal of these micropollutants with enhanced coagulation, despite fairly good removals of TOC and DOC.

5.1.6 Other determinands

Enhanced coagulation with ferric chloride and alum generally gave rise to colour removal of between 50% and almost 100% depending on the dose and the nature of the water. These results have been confirmed in the pilot-plant studies where the colour was reduced from values as high as 11,5° Hazen to less than 1° Hazen at ferric chloride concentrations of between 6 and 30 mg/*l* (i.e. between 2 and 5 times the optimum turbidity removal dose).

Enhanced coagulation was also found to be effective for the removal of algal cells. This is to be expected as "sweep coagulation" which is similar to enhanced coagulation has been used for many years for algal cell and particle removal from water. No differences have been observed between *Microcystis* and *Anabaena* in regards to the ease with which they can be removed by enhanced coagulation. Pilot-plant studies have confirmed the laboratory tests with algal cell removals in excess of 90% and very often complete removals occurring at ferric chloride doses of between 10 and 30 mg/*l* (**Figure 9)**.

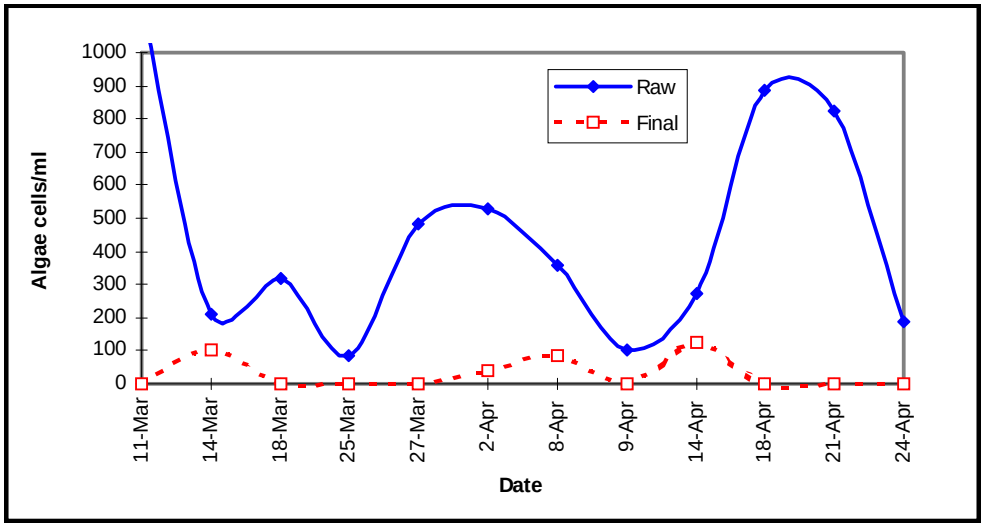

Figure 9: Pilot-plant results depicting the effect of enhanced coagulation on the algal cell concentration.

5.1.7 Fractionation of NOM

Fractionation of the NOM was only carried out on the industrially polluted water since the observation of trends was very difficult in the low DOC waters. The NOM of this water was generally found to consist of almost equal quantities of hydrophilic and hydrophobic compounds, with the hydrophobic compounds usually in slightly higher concentrations. However, this water source was fairly variable and the

composition of NOM was very different in some samples. Recoveries of DOC after XAD-16 fractionation were generally around 80%.

Enhanced coagulation was usually slightly more effective in removing the hydrophobic fraction, with removals of between 50 and 75% being possible, although removal of the hydrophilic DOC compounds was also fairly good (35 to 70% being possible). A number of references can be found supporting the fact that hydrophobic organic compounds are more readily removed than the hydrophilic compounds during coagulation (Babcock and Singer, 1979; Jekel, 1985; Collins *et al.*, 1986; Sinsabaugh *et al.*, 1986). The humic compounds have always been considered the more important fraction in terms of THMFP (Babcock and Singer, 1979; Collins *et al.*, 1986), however, more recently evidence has emerged to suggest that a significant amount of the DBP formed during disinfection can be formed from the hydrophilic compounds (Owen *et al.*, 1995) and that in addition to this, they may be responsible for a greater proportion of the BDOC.

Ozonation was found to increase the proportion of hydrophilic DOC relative to the hydrophobic, but usually by less than 10%. Furthermore ozonation was often found to have a detrimental effect on the removal of the hydrophobic compounds by enhanced coagulation, although removal of the hydrophilic compounds did not appear to be affected. This implies that the hydrophobic DOC oxidised by ozone is the fraction which is most easily removed during coagulation. It could also be due to ozone reducing the molecular weight and increasing the polarity of the hydrophobic DOC (Edwards *et al.*, 1994; Jekel, 1994; Reckhow and Singer, 1991), both of which would adversely affect its removal by coagulation (Edwards *et al.*, 1994; Jekel, 1994). Krasner and Amy (1995) found that coagulation removed less TOC from pre-ozonated waters compared to the same waters prior to ozonation and they explained this by an increase in the hydrophilic fraction of NOM after ozonation. Owen and co-workers (1995) also showed that NOM removal after ozonation may be more difficult, despite the fact that pre-ozonation can often enhance turbidity removal.

5.2 Effect of pH on Enhanced Coagulation

Tests were carried out to assess the effect of pH on enhanced coagulation. It was found that the optimal pH for turbidity removal is somewhat higher than that for optimal organic carbon removal when using the inorganic coagulants. The optimal pH value for turbidity removal was between 5,5 and 7 when using ferric chloride and between 6 and 7 when using alum, which is in agreement with literature (Water Treatment Plant Design, 1978). Organic carbon removal appeared best at a pH of around 5 when using ferric chloride and at between 5 and 5,5 when using alum, which is in agreement with the findings of Randtke (1988). If the pH dropped below 4 solubilisation of iron and manganese occurred and removal of turbidity, UV and organic carbon concentrations deteriorated.

The pH was, unexpectedly, found to affect NOM removal when using a polymeric coagulant, with the optimum pH being around 5. NOM removal with an organic polymeric coagulant was generally rather poor (not more than 10%) at the ambient pH of the water (7 to 8). However, DOC removals could be increased by 15 to 25% by reducing the pH to around 5 using acid, without any adjustment to the coagulant dose.

Using pH depression the DOC removals could also be increased by between 15 and 25% when using the inorganic coagulants. Significant increases in DOC removal could be obtained by keeping the coagulant dose constant and reducing the pH of the water with acid (acid was added prior to coagulant to produce a pH after coagulant addition of approximately 5 for ferric chloride and between 5 and 5,5 for alum). For example an alum concentration of 10 mg/*l* when used to treat a water with a DOC concentration of a little over 7 mg/*l* produced a final treated water with a pH of 7,3 and a DOC of 7,3 mg/*l* (i.e. no DOC removal had been effected). Adding acid to the water prior to coagulation to produce a final treated water with a pH of 5,6, resulted in a DOC of 5,7 mg/*l*, a decrease in DOC of 22%. Krasner and Amy (1995) observed a similar effect. They found during laboratory studies that a particular water required 47 mg/*l* alum to achieve a TOC removal of 39%, whereas it was possible to achieve a 36% TOC removal from the same water using only 13 mg/*l* alum and approximately 34 mg/*l* sulphuric acid to depress the pH. These results imply that significant coagulant cost savings are possible if pH adjustment is used. However, the cost of the acid used and the additional complication of adding two chemicals to the system needs to be born in mind.

When no pH adjustment was made, the turbidity was usually found to start increasing again once the pH had dropped to approximately 5 and 5,5 when using ferric chloride and alum respectively. In tests where sodium hydroxide was added prior to ferric chloride coagulation in order to prevent the pH from dropping below 5 it was possible to obtain TOC/DOC removals at much higher ferric chloride doses than is possible without pH adjustment. Under these conditions the UV extinction and turbidity were also found to only start increasing at much higher coagulant concentrations than was the case without pH adjustment. However, the benefit of this in regards additional TOC/DOC removal does not appear from initial tests to warrant the added inconvenience of pH adjustment.

5.3 Effect of Ozone and Permanganate on Enhanced Coagulation

5.3.1 Effect of ozone

Pre-ozonation of water samples prior to enhanced coagulation with ferric chloride, alum and a polymeric coagulant was carried out in order to determine whether it would be possible to further increase the removal of organic carbon which could be obtained using enhanced coagulation alone. Although ozone was very good for the removal of geosmin, MIB and atrazine (**Figure 10)**, the results of these investigations indicate that there would be no significant benefit from pre-ozonation in terms of organic carbon removal, ozone having little or no impact on the effect of enhanced coagulation on most NOM parameters.

In many cases there was no significant difference in the THMFP, TOC and DOC removal obtained using enhanced coagulation with or without pre-ozonation. It was however possible in some instances to increase TOC/DOC removal achievable with enhanced coagulation alone by between 10 and 15% if the water was first ozonated (**Figure 11)**. However, the capital and running costs of installing an ozone plant could not be justified by such a small improvement in organic carbon removal.

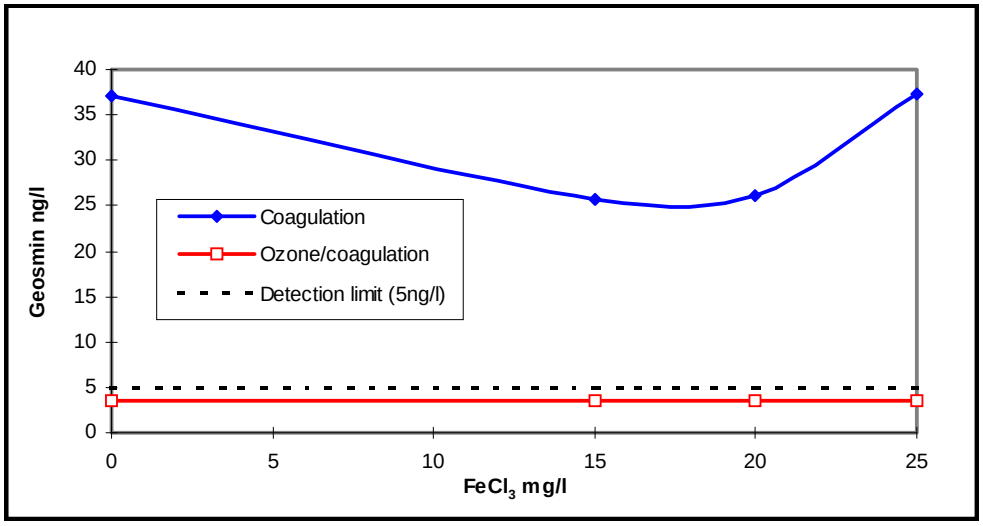

Figure 10: **Effect of pre-ozonation and enhanced coagulation on the geosmin concentration of a eutrophic water (Inanda Dam water containing 10 000 *Microcystis* cells/m*l*).**

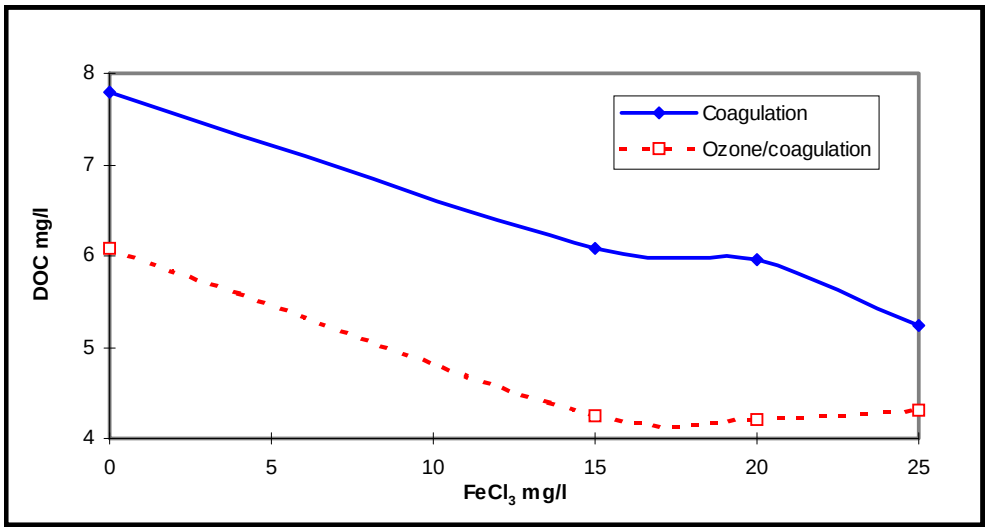

Figure 11: **Effect of pre-ozonation and enhanced coagulation on the DOC of a eutrophic water (Inanda Dam water containing 10 000 *Microcystis* cells/m*l*).**

5.3.2 Effect of permanganate

Permanganate was not found to impact on enhanced coagulation in terms of TOC, DOC, UV absorbance or colour removal. It behaved in much the same way as ozone, having no obvious affect on the removal of these parameters by enhanced coagulation. A typical set of data graphically depicting this appears in **Figure 12**. Permanganate was not found to significantly affect the concentration of micro-pollutants, in contrast to ozone, which could effect good removals of these contaminants (see **Figure 13**).

It was noted that the addition of permanganate resulted in an increase of manganese in the final treated water, while iron levels increased in water which had been treated with ferric chloride. Solubilisation of iron obviously occurs at the low pH values utilised during enhanced coagulation.

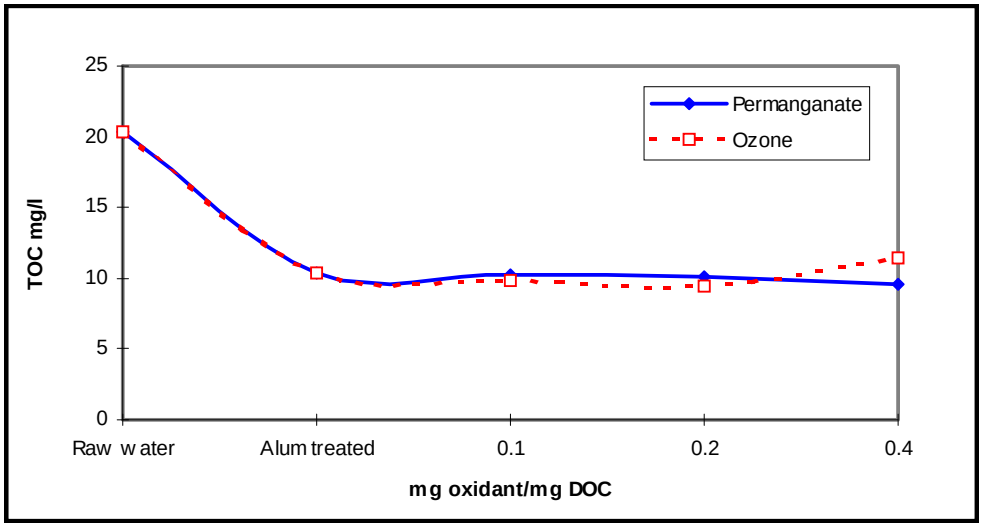

Figure 12: Impact of ozone and permanganate on the effect of enhanced coagulation (alum) on TOC.

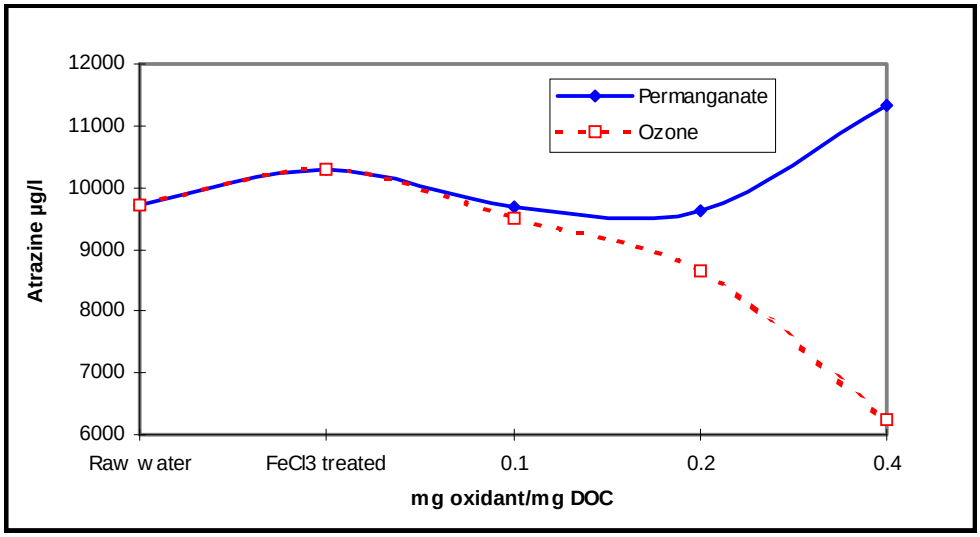

Figure 13: Effect of ozone and permanganate on the concentration of atrazine.

5.4 Enhanced Coagulation using Magnetite

Laboratory tests in which magnetite was used for enhanced coagulation were also carried out. Magnetite, which is sold under the trade name of Sirofloc, is used as an alternative to conventional methods for potable water treatment and has been found to be effective for colour removal. Magnetite is used for water treatment in a process whereby the surface charge of the magnetite is rendered positive by lowering the pH so that negative particles in the water can be removed. The magnetite is then removed magnetically and regenerated under basic conditions. It was thought possible that the highly structured crystalline nature of magnetite may allow adsorption of organic compounds in addition to those removed electrostatically during coagulation.

Magnetite was used in concentrations of between 250 mg/*l* and 200g/*l*, both with and without the addition of polymeric coagulants. Three different polymeric coagulants were used, namely an anionic polyacrylamide, a cationic polyamine (PA) and a cationic blended coagulant consisting of dimethyldiallylammonium chloride and polyaluminium chloride (DMDAAC/PACl).

When used on an industrially polluted water, magnetite on its own could remove TOC/DOC by as much as 45 to 50%, but only at concentrations of between 60 and 200g/*l*, which due to the nature and weight of the magnetite were difficult to handle. However, magnetite doses as low as 250 to 500 mg/*l* produced TOC/DOC removals of between 30 and 35%. In other words, an increase in dose of between 100 and 1000 times was required for an additional 10 to 20% improvement in TOC/DOC removal. In the case of waters low in organic carbon content, the TOC/DOC removal obtained using magnetite was never more than 10%. This may be due to the fact that the organic carbon content of these waters is stabilised as a result of extended periods of impoundment compared to that of the industrially polluted water which was collected from a river.

THMFP removal was poor, less than 15% being obtained even at concentrations of up to 5 g/*l*, while reduction in UV absorbance was generally only significant at fairly high magnetite concentrations (above 5 to 10 g/*l*). Fairly good colour removal could be obtained, but only at very high magnetite concentrations (usually above 50 g/*l*).

The addition of polymeric coagulants was not found to significantly improve the performance of magnetite. More interestingly it was found that when using up to 40

mg/*l* of the PA or DMDAAC/PACl coagulants together with 1000 mg/*l* magnetite DOC removals of 40 to 50% were obtained, while the polymeric coagulants used at the same concentrations but without magnetite could still yield DOC removals of around 35% (see **Figure 14**). The laboratory tests indicated that magnetite will not be a viable option for enhanced coagulation treatment.

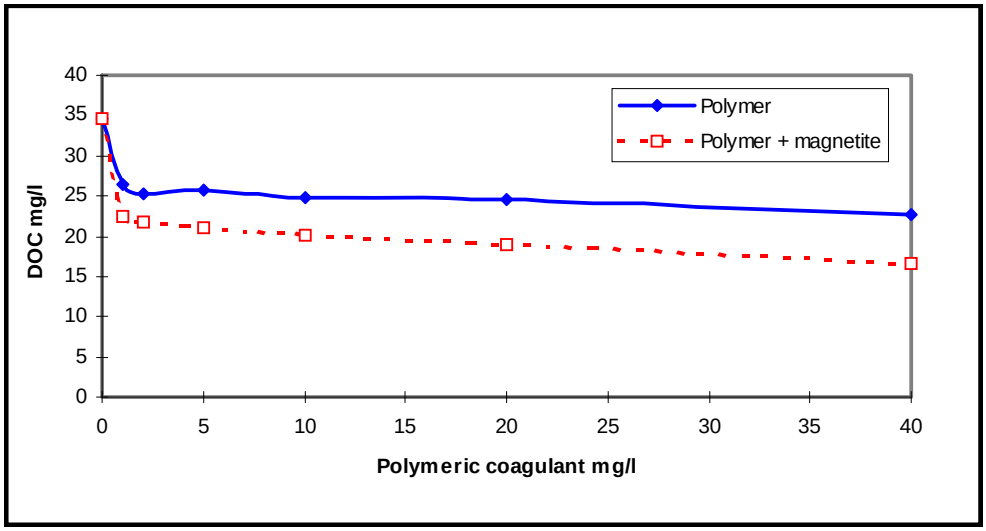

Figure 14: Effect of a polymeric coagulant both with and without magnetite (1000 mg/*l*) on the DOC of industrially polluted water.

5.5 Enhanced Coagulation Compared to Advanced Treatment Processes

The present project was carried out in conjunction with another project funded by the Water Research Commission to investigate the use of advanced water treatment processes including pre-ozonation, advanced oxidation and GAC or biologically activated carbon (BAC) (WRC Project K5/694/1, *The Treatment of Eutrophic Waters Using Pre- and Intermediate Ozonation, Peroxone and Granular Activated Carbon*). In this section reductions obtained in DBP precursors, pesticide/herbicide contaminants, taste and odour compounds and other NOM surrogate parameters using enhanced coagulation are compared to those achievable using ozone or advanced oxidation followed by GAC.

The same waters were used for both projects, namely a water low in organic content, eutrophic water containing either *Microcystis* or *Anabaena* cyanobacteria at concentrations of between 10 000 and 500 000 cells/m*l* and a water high in organic pollutants from an industrial source.

It was possible with enhanced coagulation to obtain in the region of 40 to 50% reductions in THMFP, with removals of between 50 and 75% in DBP being cited in the literature (Amy and Chadik, 1983; Babcock and Singer, 1979; Dempsey *et al.*, 1984; Glaser and Edzwald, 1979; Hubel and Edzwald, 1987; Hundt and O'Melia, 1988; Kavanaugh, 1978; Reckhow and Singer, 1984; Semmens and Field, 1980). Enhanced coagulation is therefore far more effective for THM precursor removal than ozonation alone, which results in little or no reduction in THMFP. However, pilot-plant studies in which final treated water was ozonated prior to filtration through GAC brought about as much as a 40% reduction in THMFP. Enhanced coagulation therefore compares very favourably with the more advanced treatment options of ozone and GAC in terms of THMFP removal.

TOC and DOC removals of between 20 and 40% and even up to 50% were achieved in the laboratory using enhanced coagulation for the treatment of waters which had low to moderate TOC and DOC concentrations (i.e. 4 to 8 mg/*l*). These removals were obtained at inorganic coagulant doses in the region of 1,5 to 5 times the concentration required for optimal turbidity removal. In pilot-scale tests reductions in TOC and DOC of between 55 and 60% were achieved at coagulant concentrations in the region of 2 to 5 times that required for optimal turbidity removal. Enhanced coagulation was even more effective in TOC and DOC reduction in industrially polluted waters, removals of over 60% being possible at coagulant concentrations of between 1,5 and 7 times the optimal dose for turbidity removal.

Ozonation alone was generally not effective for TOC and DOC removal and pilot-plant tests indicated that TOC and DOC removals after conventional treatment followed by ozonation and GAC filtration were in the region of 15 to 30%, which is no better than that achieved using enhanced coagulation.

Enhanced coagulation was effective in reducing BDOC as well, good removals (30 to 50%) even being obtained at the optimal coagulant doses in terms of turbidity removal. It was possible to obtain between 70 and 90% removal when using between 2 and 5 times the optimal turbidity removal dose. In contrast to this, ozonation increased the BDOC concentration, but conventional treatment followed by ozonation and GAC filtration could bring about good removals of BDOC, in excess of 80% according to the results of the pilot-plant investigation. The results imply that

enhanced coagulation may provide as effective BDOC removal as the more advanced treatment options but far more cost-effectively.

Enhanced coagulation yielded good reductions in colour (up to 100% depending on the coagulant dose and the nature of the NOM present in the water) and algal cells (90 to 100% at doses of 2 to 5 times the optimal turbidity removal dose). This is to be expected as "sweep coagulation" which is similar to enhanced coagulation has been used for many years for algal cell and particle removal from water. These results compare favourably with those of advanced treatment processes where removals of the same order of magnitude were possible.

Enhanced coagulation was not effective in removing geosmin, 2-MIB or atrazine, in contrast to ozonation which could effect removals in excess of 70% at applied ozone concentrations of 0,5 to 1 mgO_3/mg. These results indicate that enhanced coagulation is as effective as the more advanced water treatment systems for NOM removal, but if micro-pollutants are present, ozonation and/or GAC would probably be required.

5.5 Summary of Conclusions

The following conclusions were drawn from the results of this investigation:

- Inorganic coagulants are generally better for removal of NOM using enhanced coagulation.
- Removals of up to 60% in TOC/DOC, up to 40% in THMFP and between 70 and 90% in BDOC can be obtained using enhanced coagulation without pH adjustment, although this is dependent on the nature of the water.
- Optimal NOM removal occurs at between 1,5 and 7 times the optimal coagulant concentration for turbidity removal. This is also dependent on the nature of the water.
- Magnetite does not appear to be a viable option for enhanced coagulation as it does not offer any significant benefits over other coagulants.
- Enhanced coagulation is not generally good for the removal of geosmin, MIB and atrazine.
- UV extinction correlates well with turbidity, TOC and DOC.
- Pre-ozonation is effective for geosmin, MIB and atrazine removal, but does not offer any other benefits relative to enhanced coagulation in terms of TOC and DOC removal.

6. Guidelines for Enhanced Coagulation

The following guidelines are included for implementation of enhanced coagulation:

- Enhanced coagulation is effective for TOC, DOC, BDOC, THMFP and colour removal, but not for the removal of micro-pollutants and taste and odour compounds. This needs to be considered when deciding on the most appropriate treatment options for a particular situation.
- The inorganic coagulants such as ferric chloride and alum are generally more effective than the polymeric coagulants for enhanced coagulation applications.
- The optimal coagulant dose for enhanced coagulation effects is generally between 1,5 and 7 times the optimal coagulant dose for turbidity removal. These doses need to be assessed using laboratory, pilot-plant or full-scale tests.
- Alkalinity will adversely affect enhanced coagulation. Depressing the pH using acid to between 5 and 5,5 will increase the NOM removals achievable using enhanced coagulation.
- If determination of TOC/DOC is not possible, turbidity or UV absorbance (254 nm) can be used to determine optimal organic carbon removal.

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