University of Nottingham
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A study of hybrid clarification-filtration processes for potable water treatment

By

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Dedicated to my Mother and Father

Contents

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To all my friends in Nottingham

Abstract

This research investigates the removal of natural organic matter (NOM) from low turbidity waters by optimising an integrated coagulation and membrane filtration process. In conjunction with a regional water utility, the feasibility and operability of pre-coagulation with ultrafiltration membrane units, is investigated at both the fundamental and applied levels.

The pH of coagulation greatly affects the growth of flocs. Although flocs are produced over the range of pH values, there is a significant improvement in performance at the optimum pH. The results show that for ferric sulphate, the optimum pH value for coagulation was 4.8; for ferric chloride the optimum pH value was 5.0; and for alum the optimum pH value was 6.

Manipulation of the mixing regime during orthokinetic flocculation allows control of the final floc size. A high shear rate ($447s^{-1}$) induces greater particle collision and micro-floc formation, allowing an increased rate of growth during slow mixing. A mixing regime of 60 seconds rapid mixing (shear rate $G = 447\ s^{-1}$) followed by 3 minutes slow mixing (shear rate $G = 20\ s^{-1}$) is required for flocculation of the NOM and adequate enmeshment and removal of excess iron.

Experiments conducted with the optimised coagulation regime and a Norit hollow fibre ultrafiltration membrane, operated in dead-end mode, leads to significant fouling. The results for the submerged Zenon ultrafiltration membrane also indicated membrane fouling, when the coagulation regime was optimised for NOM reduction and iron removal. Changing the coagulation regime altered the level of membrane fouling.

It can be concluded that the optimum coagulation conditions in conventional water treatment are not always the optimum conditions for coagulation with ultrafiltration treatment and the unconventional coagulation conditions can be much more effective, than the conventional ones, in the context of membrane filtration, depending on the raw water characteristics.

List of Symbols, Abbreviations and Notation

G Shear rate (s^{-1})
N_p Impeller number
ρ Fluid density
N Impeller rotational speed
D Impeller diameter
μ Fluid dynamic viscosity
$\bar{\varepsilon}$ Reactor average turbulent energy dissipation rate
v Kinematic viscosity of the fluid.
BV Bed volume
CA Cellulose acetate
CSIRO Commonwealth Scientific and Industrial Research Organisation
DAF Dissolved air flotation
DBP Disinfection by-product (µg L)
DOC Dissolved organic carbon (mg L)
DWI Drinking Water Inspectorate
FAF Fulvic acid fraction
GAC Granular activated carbon
HAA Haloacetic acid (µg L-1)
HAF Humic acid fraction
MF Microfiltration
MIEX® Magnetic ion exchange
MW Molecular weight (Daltons)
MWCO Molecular weight cut-off
NF Nanofiltration
NOM Natural organic matter (mg L)
PA aromatic polyamide
PAC Powdered activated carbon
PACl Polyaluminium chloride
PDA Photometric dispersion analyser
RO Reverse osmosis
TFC Thin-film composite

THM Trihalomethane (µg L-1)
THMFP Trihalomethane formation potential (µg mg C)
TOC Total organic carbon (mg L)
UF Ultrafiltration
UV Ultraviolet (m-1)
ZP Zeta potential (mV)

Chapter 1

Introduction

The natural colour of upland waters is mainly due to organic acids, in the form of soluble and colloidal-size macromolecules. These molecules, known as natural organic matter (NOM), derive from decaying vegetation and often lead to an orange/yellow tint since a large proportion are soluble (Gregor J. E. et al., 1997). The concentration of NOM in upland waters in the UK has been steadily increasing in recent years, very possibly as a result of systematic climate change. Removal of these NOMs is critical to meeting water quality standards on Trihalomethanes (THMs); these are toxic by-products formed from residual NOMs during the chlorination and disinfection stages. In addition, health concerns over disease-causing protozoan such as *Cryptosporidium* and *Giardella* have also led to stricter standards. In the UK the limit on *Cryptosporidium* is 1 oocyst per 10 litres of finished water (D.W.I., 2003)

Many water companies would acknowledge that conventional clarification is not necessarily the most cost effective solution for the removal of natural organic matter (NOM) from upland surface water. In addition to this, there is a constant drive within the water supply industry to develop more compact treatment units – retrofitted to existing sites – and therefore occupy less land space and reduce capital costs. There is thus a driving need to find cheaper and more intensified solutions for treating upland waters. This is reflected in the current Asset Management Plan of the English and Welsh water companies (Fawcett N. D. I., et al., 2003), in which an emphasis has been placed on compact, high-rate processes. The development of the solids-contact unit, often called the up-flow clarifier, has traditionally represented such process intensification in clarification. These units combine mixing, flocculation and sedimentation into a single structural unit (Figure **1.1**).

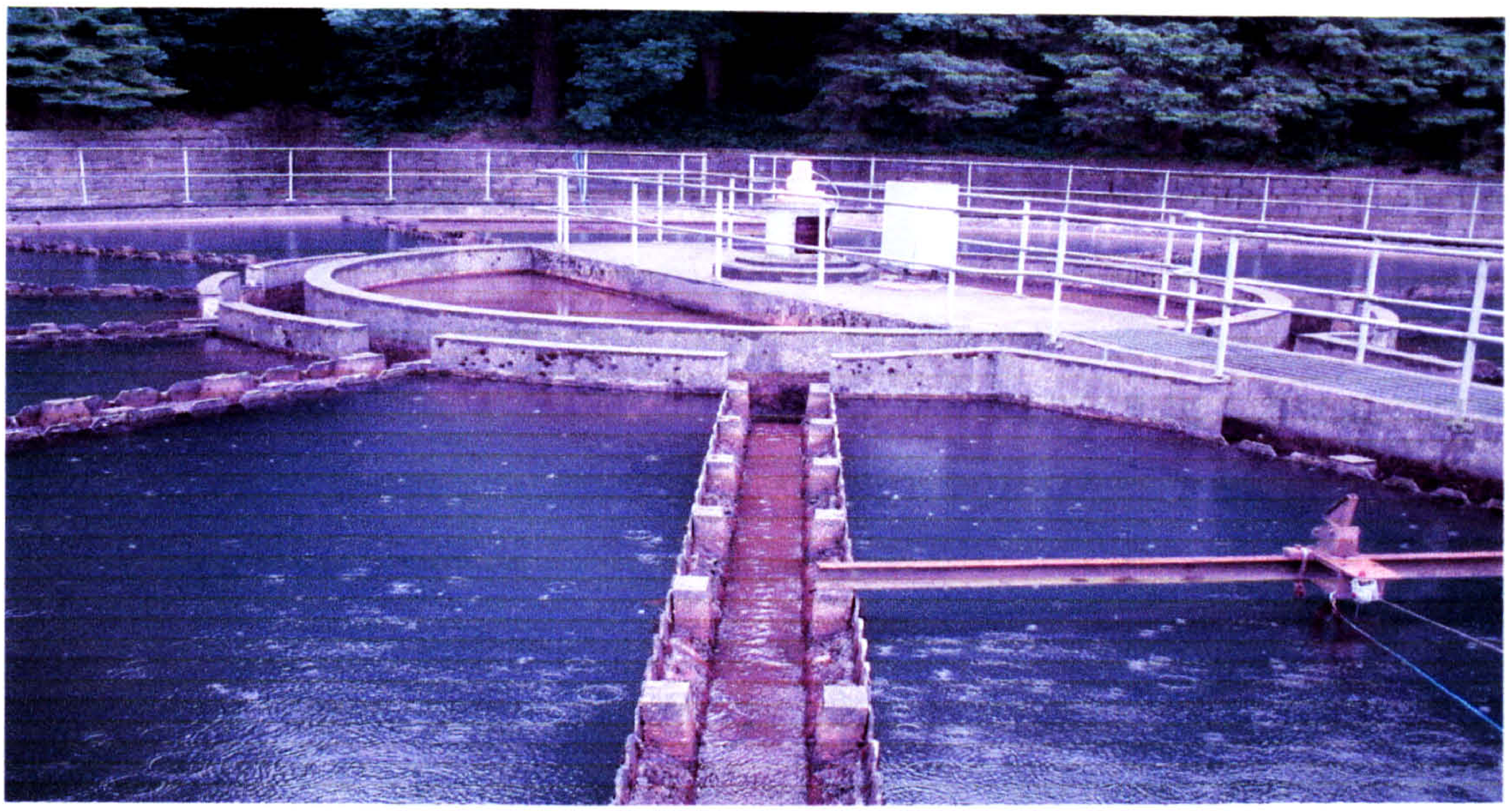


Figure 1.1: Solids Contact Unit for Clarification (Courtesy: Severn Trent Water)

Clarifiers rely on the use of a large tank for sedimentation of flocculated solids. The basin normally contains separate chambers for mixing and settling, the two steps critical in achieving good clarification. An initial period of turbulent mixing is needed for contact between the coagulant and suspended solids. This is followed by a period of gentle stirring, which helps to increase particle collision and floc size in a process known as orthokenetic flocculation. Retention times are typically between 3 and 5 minutes for initial mixing, 15 to 30 minutes for orthokenetic flocculation, and 4 to 6 hours for settling. The water passes out over the top of the weir, while the flocculated particles settle to the bottom. The accumulated sludge is scrapped into a sludge collection basin for removal and disposal. By maintaining a large volume of flocculated solids in the system, the flocculation of incoming solids is enhanced because of an increased frequency of inter-particulate collision; typically, solids volume in the contact zone varies from 5 to 50%.

In sludge blanket clarifiers, mixing and flocculation are achieved in the centre compartment with agitation and gentle stirring provided by pitched blade impellers. Such units are ideally suited to feed water with relatively constant quality, such as lake or reservoir and well waters. While the hydraulic loading rate, (the flow to a treatment plant or treatment process), for basic sedimentation is between 1 and 1.5 m/h, rates of up to 4 m/h can be achieved with sludge blanket clarifiers.

Although the process seems relatively simple, especially in relation to many chemical manufacturing operations or unit processes, there are a number of potential operational difficulties. Excessive floc carryover is a very common problem. This is often associated with hydraulic overload or unexpected flow surge conditions. Hydraulic overload conditions are not the only causes of excessive floc carryover. Other reasons may be thermal currents, short-circuiting effects, low-density flocs and chemical feed problems. Another common problem is simply no floc formation, resulting from underfeeding of the coagulant.

The lack of a filtration system allows the introduction of flocs to downstream processes increases the risk of a treatment plant failing to meet water quality standards on THM formation. Clarifiers are also unable to guarantee the removal of protozoan such as *Cryptosporidium* and *Giardella.* This was highlighted by two serious incidents in Glasgow; in August 2002 *Cryptosporidium* was detected in the Mugdock Reservoir in Milngavie. As a result, approximately 140,000 Glasgow residents were advised to boil all tap water used for drinking, preparing food, brushing teeth and bathing babies. The reservoir was the source of a previous outbreak of *Cryptosporidiosis* in 2000, in which there were 90 confirmed cases, including 6 people who required hospitalisation and 1 death. Scottish Water is planning to upgrade the water treatment works at a cost of £100 million (*The Scottish Parliament - Information centre 2002).* These cases simply highlight the need for improvements in conventional water treatment methods

Membrane Enhanced Clarification

Membrane units are taking on an ever-widening role in water treatment. However, an important consideration for both potable and wastewater treatment with low-pressure membrane filters is the reduction in permeation rate due to the accumulation of colloidal and macromolecular materials on and within the membrane. A strategy for improving membrane performance would be to combine it with a coagulation pre-treatment stage; thus colloids capable of entering the pores are coagulated to produce particles rejected by the membrane **(Fig 1.2)**.

This would have the following advantages:

- Permeate flux is increased by: -
    1. Reducing foulant penetration
    2. Forming a protective porous cake on the membrane surface
    3. Decreasing the accumulation of foulants near the membrane.
- Filtered water quality is improved.
- Two unit operations are combined into one unit, i.e. coagulation and filtration (no need for sedimentation), reducing footprint.

Studies have indicated that the combination of microfiltration (MF) or ultrafiltration (UF) with upstream coagulant dosing is beneficial (Judd S. J. and Hillis P., 2001); combining them yields significant flux enhancements over MF/UF alone, particularly when the waters are laden with NOM.

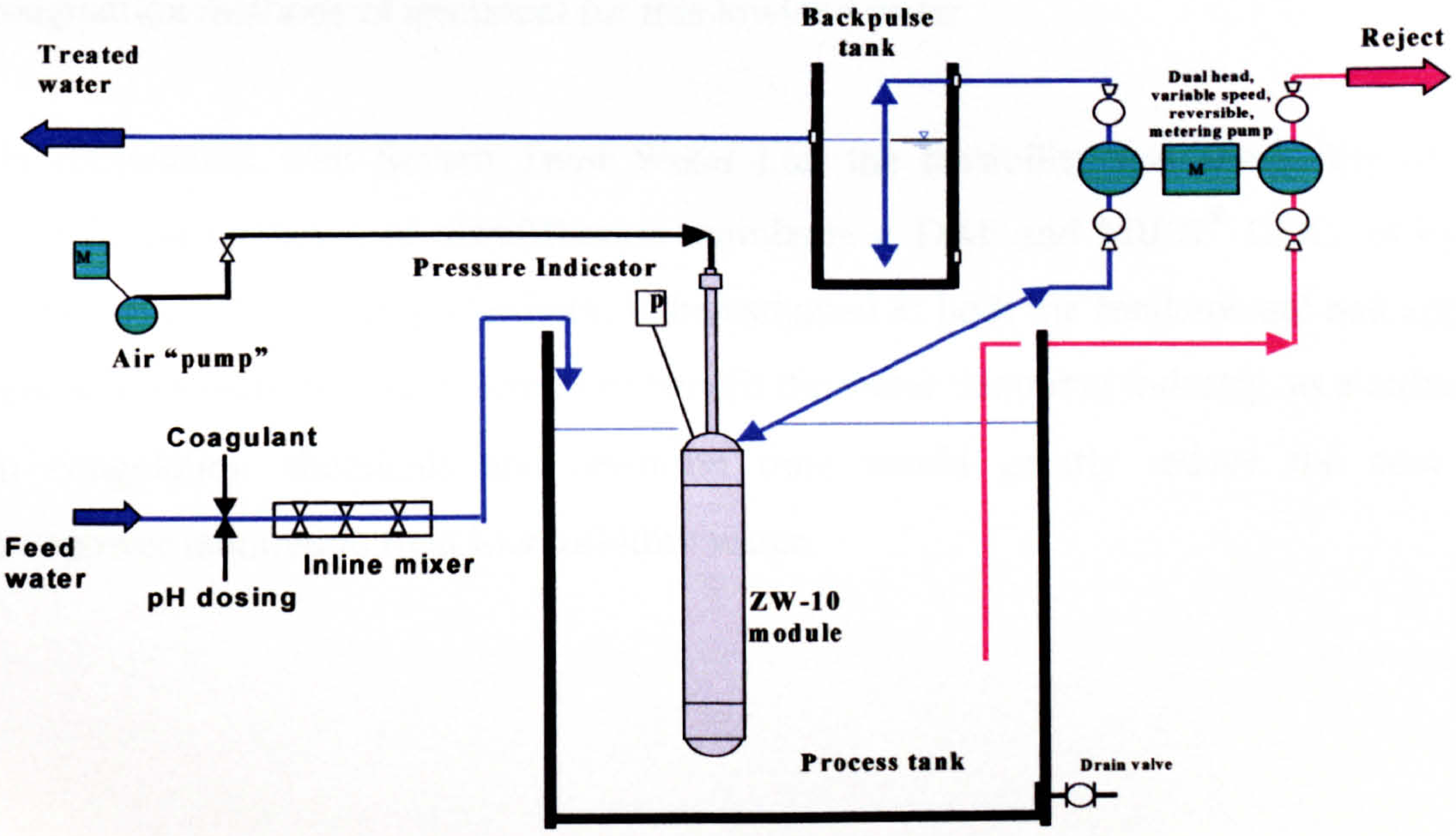


Figure 1.2: Schematic of Membrane-Enhanced Coagulation Unit

The use of membrane filtration also permits significant advantages over conventional clarification. The flocculation and settling times can be significantly reduced to the order of minutes rather than hours; this is because the pore size is sub-micron, so flocs really only need to grow to the order of microns in size rather than the larger sizes required for sedimentation (It should be noted that the flocs must be large enough to remove all coagulant). Settling tanks as such are not required, though the sludge must still be disposed off. All of this leads to significant process intensification; potential loading rates are on the order of 100 m/h. Clearly, there is a strong technical and economic synergy and a significant future potential.

This thesis investigates the removal of natural organic matter from low turbidity upland waters by optimising an integrated coagulation and membrane filtration process, specifically the impact of excess coagulant on membrane performance, which is exacerbated during periods of low temperatures. Research was also conducted on the use of pre-coagulation with ultrafiltration membranes to treat lowland waters. This latter water contained low turbidity and colour, but contained significant levels of total organic carbon (TOC) that were difficult to remove using conventional treatment. The investigation also incorporated a magnetic ion exchange (MIEX® DOC) pilot unit, as well as a dissolved air flotation (DAF) pilot unit to study alternative enhanced coagulation methods of treatment for this lowland water.

In conjunction with Severn Trent Water Ltd, the feasibility and operability of pre-coagulation upstream of ultrafiltration membranes; DAF and MIEX® DOC, as hybrid replacements for existing clarifiers, is investigated at both the fundamental and applied levels. This work has the potential to benefit the water treatment industry, as a reduction in coagulation chemicals and retention time would greatly reduce the cost and manpower required to treat low turbidity water.

Chapter 2

Review of Literature

2.1 Introduction

Many water companies would acknowledge that conventional clarification, possibly combined with another process such as powdered activated carbon adsorption, is not necessarily the most cost effective solution for NOM removal. In addition to this, there is a constant drive within the water supply industry to develop more compact treatment units – retrofitted to existing sites – and therefore occupy less land space and reduce capital costs. There is thus a driving need to find cheaper and more intensified solutions for treating upland waters. This is reflected in the current Asset Management Plan of the English and Welsh water companies (Fawcett N. et al., 2003) in which an emphasis has been placed on compact, high-rate processes. The application of membrane units is a potential solution.

2.2 Membrane classification

There are four categories of membranes used for the treatment of drinking water; these are Reverse Osmosis (RO), Nanofiltration (NF), Ultrafiltration (UF) and Microfiltration (MF). The type of membrane used varies widely depending on the quality of the water to be treated, particularly on the size of material to be removed. The filtration spectrum (**Fig 2.1**) is a chart, which shows the size range of particles and the type of filtration used for each range. There are five main size categories of particles: macro, micro, macro molecular, molecular and ionic particles.

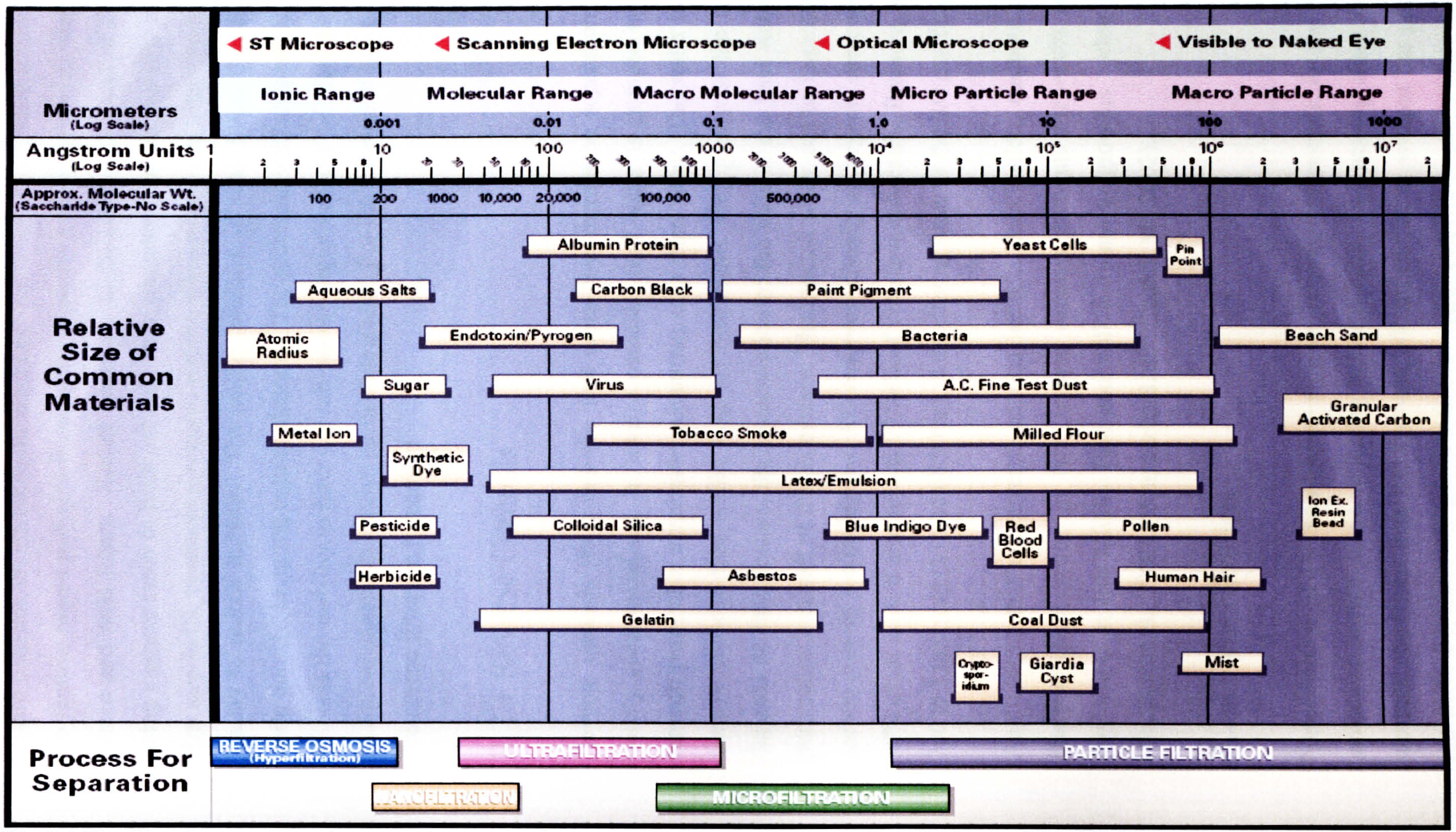


Fig 2.1 The filtration spectrum (source: www.osmonics.com

Macro particles are visible to the naked eye and range in size from 50μm to 1000μm. To remove macro particles from water, there are various treatment methods including screen and sand filters. Screen filters are at the rudimentary end of filtration media, using a coarse mesh to filter out only large particles. They are usually employed as the first step in the treatment process to remove silicates and leaf litter. Sand filters are used mainly to reduce turbidity. The major drawback of sand filters is that they can clog quite quickly, requiring regular cleaning. The problems with all types of macro particle filters is the inability to filter out sub-micron impurities and therefore are used primarily as a pre-treatment to remove particulate matter. For the removal of sub-micron particles, membrane filtration is required.

2.2.1 Reverse Osmosis

Reverse osmosis (RO) was the first cross-flow membrane separation process to be widely commercialised. In reverse osmosis, feed water is pumped at high pressure through permeable membrane, separating salts from water. The water is pre-treated to remove particles that would clog the membrane. The quality of the water produced depends on the pressure, the concentration of the salts in the feed water, and the salt permeation constant of the membrane. The product water can be improved by adding a second pass of the membrane. RO removes virtually all organic compounds and 90 to 99% of all ions. It also rejects 99.9+% of viruses and bacteria. Pressure, on the order of 200 to 1,000 psig (13.8 to 68.9 bar), is the driving force of the RO purification process.

Applications that use reverse osmosis include: desalination, electronics rinsing, and pharmaceutical water. In fact, reverse osmosis accounts for ~10% of fresh water production in the Middle East and will continue to grow as technology improves (Nicolaison B., 2002), (Bouguecha S. and Dhahdi M., 2002).

2.2.2 Nanofiltration

Nanofiltration (NF) membranes remove organic compounds in the 300 to 1,000 molecular weight range, rejecting selected salts, and passing more water at lower pressure operations than RO systems. NF softens water without the pollution of salt-regenerated systems and provides unique organic desalting capabilities.

Nanofiltration is used for particles in the molecular range (0.05 m to 0.005 m). These size particles are only visible with a scanning electron microscope. Sugar, synthetic dye, and endotoxins are particles rejected within this range as well as smaller particles of colloidal silica, viruses and larger charged ions such as hardness.(Liikanen R. et al., 2003).

As NF membranes are used for treating soft waters, the ability to remove hardness is undesirable. To overcome this problem, membranes have been designed with a lower divalent ion retention coupled with high organics removal and permeability (Ikeda k. et al., 1988).

In potable water treatment, Nanofiltration can used to treat groundwater where the levels of NOM are very low (Fu P. et al., 1995), or as a finishing tool when the raw water has been pre-treated to reduce the NOM levels (Liikanen R. et al., 2003).

2.2.3 Ultrafiltration

Ultrafiltration rejects contaminants in the range of 1000 daltons to 0.1 micron particles. Because of the larger pore size in the membrane, UF requires a much lower operating pressure: 10 to 100 psig (0.7 to 6.9 bar). UF removes organics, bacteria, and parasites while allowing most ions and small organics to permeate the porous structure (Hagen K., 1998).

Industry uses ultrafiltration for many different applications including: pre-treatment for other purification systems where organics are not removed (such as ion exchange systems), gelatin and protein concentration in the pharmaceutical industry, sugar clarification in the food and beverage industry, cheese whey concentration, oily waste concentration in heavy industrial applications, and drinking water applications as well as many others.

Ultrafiltration is not as fine a filtration process as nanofiltration, but it also does not require the same energy to perform the separation. Because UF has larger pores, it is the least costly to operate, requiring fewer membrane elements and lower operating pressure than the other two processes. As the pores get smaller, as does the cost of operation increases. The capital costs tend to be relatively similar since a large portion of these costs are associated with piping, frames, controls, etc.; all of which are related to the quantity of water to be processed.

2.2.4 Microfiltration

Microfiltration is the oldest and most widespread membrane technology; the membranes have a micro-porous barrier layer that removes small particles based on a sieve effect. As all particles larger than the membrane pore diameter are retained, MF membranes are classified as absolute filters; typically rated in the 0.1 to 10μm range. Microfiltration membranes used in the treatment of drinking water are particularly suited to the removal of suspended solids, especially bacteria, algae, protozoa, such as *Giardia* and *cryptosporidium* (Jacangelo J. G. et al., 1997),(MacCormack A. B., 1995).

2.3 Membrane materials

The wide range of water recovery applications comprises a variety of fluid environments, some of which may be detrimental to certain polymeric materials and the characteristics of membrane. Operating conditions such as temperature, pressure, solution pH and chemical compatibility must therefore always be considered. No one polymer will withstand the environments of all the possible water recovery applications, so several different membrane materials should be investigated to select the optimum for each situation.

Reverse Osmosis polymers currently available include the asymmetric membranes: cellulose acetate (CA) and aromatic polyamides (PA-type). Also available are the newer thin-film composite membranes (TFC), of which aromatic polyamide (PA) on a polysulfone substrate is the best known.

The CA membranes tolerate chlorine at levels used for microbial control, while even low levels of chlorine will destroy PA membranes. However, the PA membranes produce both higher rejection and flux, and tolerate a wider pH range on a continuous basis and a higher continuous temperature than CA membranes.

Nanofiltration membranes are generally PA and CA based.

Ultrafiltration membranes are made from a wider range of more rugged polymers, since their larger pore size and "sieve" mechanism of separation allow more material choices. Cellulose acetate, polyvinylidene fluoride, and polysulfone are the most common. Polysulfone UF membranes can withstand a pH range of 1 to 13, temperatures to 85°C and 25 mg/L of free chlorine on a continuous basis (X-Flow, 2004).

Materials for microfiltration membranes include everything used for RO and UF membranes, as well as polycarbonate, polypropylene and polyethylene, and therefore can have quite rugged physical and chemical characteristics

Microfiltration membrane polymers commercially available are the most numerous, due to the relative ease of achieving the required pore size for MF compared to UF and RO membranes. Polyethersulphone, polypropylene and cellulose acetate are among the more common MF polymers, and their broad chemical compatibility characteristics make the MF range of membranes the most chemically stable.

Ceramic membranes have been commercially available for about 10 years and, due to their substantial cost, their acceptance is emerging slowly. These are generally alumina based and have about the same chemical resistance of the polysulfone polymer but are more heat resistant. (Bottino A. et al., 2001)

There has also been research into the use of metal membranes, combined with a pre-coagulation stage, as an alternative method for drinking water treatment. Initial results published by Leiknes T. et al., (2004) showed a treatment efficiency of >95% colour removal with a 75% TOC reduction. A detailed analysis of investment and treatment costs was not conducted which ultimately will determine the metal membranes commercial viability.

2.4 Membrane elements

Membranes themselves are either formed as flat sheets, hollow fibres, or tubular. They must be configured into elements to manage the flow streams in the membrane machines and support the membrane under the required hydraulic pressures. Flat sheet configurations include the plate-and-frame and spiral-wound design. The plate-and-frame designs allow a variety of feed and permeate channel designs but are expensive to operate and therefore only have niche applications. Spiral-wound design affords the best "all-around" characteristics of high packing density, low cost, and rugged, high-pressure operation.

Hollow fibres are used mainly for RO purification of seawater where extensive pre-treatment protects them from fouling. Hollow fibres of larger diameter (0.5 to 2 mm) are used in UF processes. They can handle high solids loading without plugging and can be back-flushed to remove foulant layers. They have gained interest in the last 15 years but since they are self-supporting homogeneous fibres, they are limited by the tensile, compressive and flexural strengths of the membrane material, which is porous. This limits the operating pressure to 5 bars transmembrane pressure (Thorsen T., 1999).

Tubular elements are large-scale versions of hollow fibres (0.6-2.5 cm diameter) with the membrane coated on the inside wall of another porous material. This support material gives the tube its strength, so higher operating pressures are possible. However, since the forces act on the tensile strength of the tube, this design usually has lower pressure limits than spiral-wound and plate-and-frame, where the compressive strength of the membrane is the limiting factor. As with the plate-and-frame design, the much higher cost per unit area of membrane, limits the tubular configuration's use. Elements are placed in pressure-bearing housings and arrayed in machines in a manner to maximize flows and minimize space and cost.

2.5 The application of membranes for the treatment of drinking water

The application of membranes, as an alternative to conventional technology for the treatment of drinking water, has increased in recent years. Economic considerations have focussed this application mainly on microfiltration membranes, which have a 40% share of the membrane market (Ripperger S. and Altman J., 2002). Initial use of ultrafiltration was hindered, as calculations concerning investment costs showed UF to be expensive when compared to the cost of alternative techniques like direct filtration (Lipp P. et al., 1998). However, due to the rapid development of this fairly new technology, capital expenditure and associated costs of UF membrane technology have decreased to make UF membranes economically viable (Fawcett N. et al., 2003). The total global sales of membrane systems worldwide are expected to rise from $7 billion this year, to $10 billion in 2009 and to 37 billion by 2015 (http://www.mcilvainecompany.com).

This increasing role of membranes in water treatment is highlighted in the number of membrane plants commissioned in the UK since membranes were first introduced in 1992 **(Table 2.1)**

Table 2.1 Number of membrane plant constructions in the UK per year

1992	1994	1995	1996	1997	1998	1999	2000	2001	2002
1	1	3	5	7	9	8	14	23	15

The Membrane Academic Industry Network (MAIN) (2003) **Appendix C**

The type of membrane used varies widely in the UK depending on the quality of the water to be treated. **Table 2.2** shows a breakdown of the type of membrane units in operation in the UK in 2003. Reverse Osmosis and Nanofiltration membranes are used to treat groundwater that has very little NOM content. Ultrafiltration and microfiltration membranes are used to treat both ground water and surface water. According to the MAIN database the estimated capacity of ultrafiltration and microfiltration membranes in the UK in 2004 was 321,400 m^3/d and 60,527 m^3/d respectively.

Table 2.2 UK membrane municipal plant

Membrane Type	Number of Plants
Microfiltration (MF)	3
Ultrafiltration (UF)	28
Nanofiltration (NF)	42
Reverse osmosis (RO)	11
MF/UF	5
Coagulation / Ultrafiltration (C/UF)	3

http://www.cranfield.ac.uk/sims/water/mem-net/uk_membrane_municipal_plant.html

The treatment by ultrafiltration and microfiltration of waters with a high NOM concentration leads to fouling of the membrane and adequate pre-treatment of the feed is essential to maintain the operability of the membrane plants (Nicolaison B., 2002).

To improve efficiency, incorporating the membranes into a process stream will increase the removal of the constituents that cause fouling. When coupled with powdered activated carbon (PAC), ultrafiltration membranes can be used to treat groundwater contaminated by micro-pollutants, such as pesticides or surface water with a high organic content (Laîné J.M. V. D., Moulart P., 2000). Tsujimoto W. et al., (1998) also showed that ultrafiltration membranes pre-treated with granular activated carbon (GAC) could be used to treat water with high NOM loading. However the use of GAC or PAC combined with membrane filtration is an expensive treatment option (Lebeau T. et al., 1998).

2.6 Natural Organic matter

The natural colour of upland waters is mainly due to organic acids, in the form of soluble and colloidal-size macromolecules. These molecules, known as natural organic matter, derive from decaying vegetation and often lead to an orangey/yellow tint in the water since a large proportion are soluble (Gregor J. E. et al., 1997). The concentration of NOM in upland waters in the UK has been steadily increasing in recent years, very possibly as a result of global climate change. Removal of NOM is critical to meeting water quality standards on Trihalomethanes (THMs); these are toxic by-products formed from residual NOM during the chlorination and disinfection stages. In addition, health concerns over disease-causing protozoan such as Cryptosporidium and Giardella have also led to stricter standards. In the UK the standard for THMs is 100μg/l at the customers tap, and 1 oocyst per 10 litres of treated water for cryptosporidium (Drinking Water Inspectorate 2003).

As this thesis investigates the removal of natural organic matter by pre-coagulation and membrane filtration, as well as treatment by magnetic ion exchange, it is important to first understand the nature of NOM. There have been many articles published on the characterisation of the physicochemical properties of NOM. **Table 2.3** details a selection of the investigations into NOM composition.

Organic matter in surface water is a diverse mixture of organic compounds ranging from macromolecules to low molecular weight compounds such as simple organic acids and short-chained hydrocarbons. Organic matter in natural waters has been arbitrarily divided into dissolved (DOC) and particulate organic carbon (POC), based on filtration through a 0.45m filter . No natural cutoff exists between these two fractions and the distinction is arbitrary, based on the filtration of the sample. The definition of terms, therefore, is operational. Overlapping the dissolved and particulate fractions is the colloidal fraction, which consists of suspended solids that are operationally considered solutes.

Table 2.3 A selection of the investigations into NOM characterisation

Reference	**Source water**	**Analytical technique**	**Conclusion / summary**
Kim H. C. & Yu M. J. (2005)	Han River Seoul Korea	XAD Fractionation FT-IR and Proton nuclear fractionation Resonance spectroscopy	The formation of THMs was highly influenced by hydrophobic fraction, while HAAFP depended more on the hydrophilic fraction
Panyapinyopol, B., T. F. Marhaba, et al. (2005)	River Bangkok Thailand	Resin absorption fractionation (DAX-8, AG-MP-50, andWA-10)	Hydrophilic neutral and hydrophobic acid were the two main precursors for trihalomethanes formation (THMFP) in this water source
Sharp, E. L., S. A. Parsons, et al. (2005).	Moor land water UK	XAD fractionation HSPEC analysis	The hydrophobic NOM fractions have a significantly higher charge density than the hydrophilic NOM fractions, whereas the hydrophilic non-adsorbed fraction has a negligible charge density
McDonald, S., A. G. Bishop, et al. (2004)	Review article	Size exclusion chromatography Nuclear magnetic resonance spectroscopy Vibrational spectroscopy Differential scanning calorimetry Pyrolysis and related techniques Capillary electrophoresis Mass spectrometry techniques Fluorescence spectroscopy Field flow fractionation Microscopic techniques	Advances in technology have greatly advanced the understanding of dissolved organic carbon and humic substances; however, innovations are needed to characterize humic substances further. As of yet there has not been any definitive structure assigned to a humic substance
Matilainen, A., N. Lindqvist, et al. (2002)	Lake Roine Finland	HSPEC	There was little seasonal variation detected in the NOM content in the raw water

Table 2.3 A selection of the investigations into NOM characterisation

Reference	**Source water**	**Analytical technique**	**Conclusion / summary**
Scott, M. J., M. Jones, et al. (2001).	Peat pools Cumbria UK	XAD fractionation	Drought conditions and seasonal climatic changes could have appreciable effects upon molecular characteristics of natural DOM
Anderson et al (2000)	Lake Terjevann Norway	Reverse Osmosis HSPEC analysis	Differing catchments vegetation effects the molecular weight distribution of the NOM
Frimmel, F. H. and G. Abbt-Braun (1999)	Different aquatic systems Germany	XAD-8 Fractionation HSPEC analysis	High molecular substances show a relatively high UV254 absorbance and the low molecular substances, especially fulvic acids, show a decreased specific UV absorbance
Gjessing, E. T., P. K. Egeberg, et al. (1999)	Various Norway	Reverse osmosis and evaporation (EVA)	The differences in the nature of the NOM, which depends on where and when it is sampled, clearly demonstrate that there is a need for better international communication between NOM scientists in order to gain sufficient knowledge about this complicated matter.
Newcombe, G., M. Drikas, et al. (1997)	Myponga reservoir South Australia	XAD and UF fractionation Flow field flow fractionation ^{13}C NMR spectrometry	The UF fractions displayed a gradual transformation from highly coloured, highly branched, high carbohydrate structures to compounds with a prevalence of long chain aliphatic carbon with a much lower carbohydrate content and colour

NOM Composition

Colloidal organic matter in natural waters is composed of living and senescent organisms, cellular exudates, and partially-to-extensively degraded detrital material, all of which may be associated with mineral phases. Generally, DOC is in greater abundance than POC, accounting for approximately 90% of the total organic carbon of most waters. DOC is composed of hydrophilic and hydrophobic fractions.

The hydrophobic fraction can be described as humic substances comprising humic acids, fulvic acids, bases (including aromatic amines) and neutrals (including hydrocarbons and high MW aldehydes). The hydrophilic fraction is composed of Polysaccharides (including amino sugars and polypeptides); Building Blocks (humic hydrolysates with molecular weight between 300 – 450 g/mol.); Neutral Amphiphilics (alcohols, aldehydes, ketones and amino acids) and low molecular weight organic acids.

Organic compounds that are aromatic in structure or that have conjugated double bonds adsorb UV light. UV absorbance at 254nm is often used as a simple surrogate measurement for DOC that is especially effective for waters containing aquatic humics (Edzwald J. K., 1993). Frimmel, F. H. and G. Abbt-Braun (1999) expanded on this statement by showing that high molecular substances show a relatively high UV254 absorbance while the low molecular substances, especially fulvic acids, show a decreased specific UV absorbance

In most upland surface waters humic substances are the main component of NOM and are composed of fulvic and humic acids. Humic acids are defined as the fraction of humic substances that are not soluble in water under acid conditions (below pH 2), but become soluble at greater pH. They are often referred to as being the high molecular weight fraction, with weights being estimated to range from 1500 to 5000 Da in streams, and from 50,000 to 500,000 Da in soils. Fulvic acids are the fraction of humic substances that are soluble under all pH conditions and are referred to as moderate molecular weight substances ranging from 600 to 1000 Da in streams and 1000 to 5000 Da in soils (Malcolm R. L. 1990).

Humic substances can be regarded as natural anionic polyelectrolytes and have various functional groups, including carboxylic and phenolic and a frame work of randomly condensed aromatic rings (Duan J. and Gregory J., 2003). The complexity of humic substances is such, that there is only speculation as to exact composition (**Fig 2.2**).

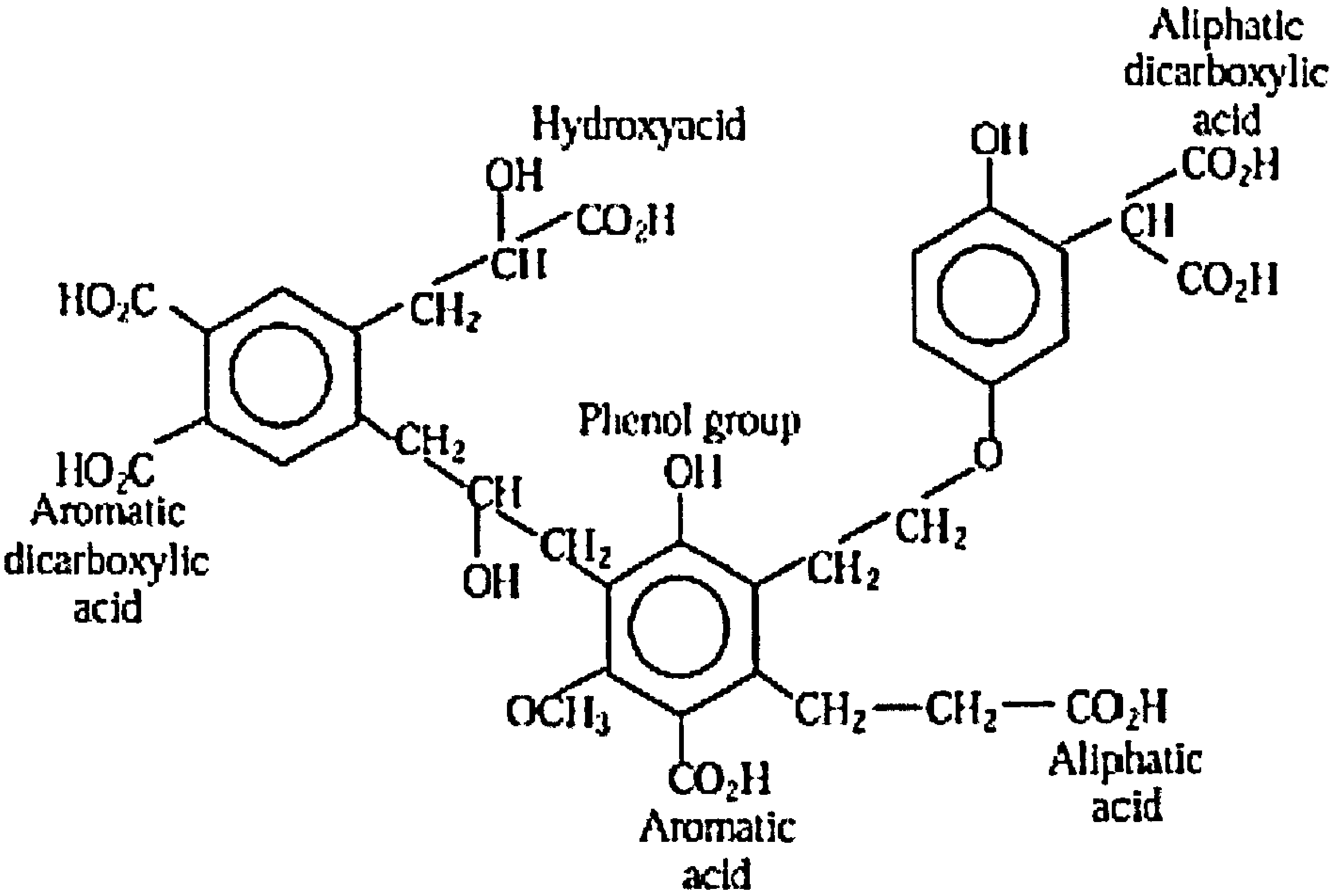


Fig 2.2 Hypothetical molecular structure of humic acid, showing important functional groups (Duan J. and Gregory J., 2003)

Although there has not been any definitive structure assigned to a humic substances, advances in technology have greatly advanced the understanding of dissolved organic carbon and humic substances. There are numerous analytical methods available of isolating humic substances, including XAD fractionation; size exclusion chromatography and nuclear magnetic resonance spectroscopy to name but a few. In an article by McDonald, S., A. G. Bishop, et al. (2004) the developments in methods of analysis including the isolation and characterization of humic substances is reviewed. .

Investigating the composition of natural organic material, Newcombe, G., M. Drikas, et al. (1997) concentrated and fractionated the NOM using UF into nominal molecular weight fractions <500, 500-3000, 3000-10000, 10000-30000 and >30000 Da. Analysing the samples utilising flow field-flow fractionation ^{13}C NMR, colour determination and potentiometric titration, Newcombe et al. stated that the UF fractions displayed a gradual transformation from highly coloured, highly branched, high carbohydrate structures to compounds with a prevalence of long chain aliphatic carbon with a much lower carbohydrate content and colour.

Impact of NOM type on conventional water treatment

Panyapinyopol, B., T. F. Marhaba, et al. (2005) using resin absorption fractionation (DAX-8, AG-MP-50, andWA-10), to characterize raw water in Bangkok stated that the dissolved organic carbon (DOC) mass distribution sequences of the six organic fractions in the raw water, from high to low, were hydrophilic neutral (HPIN), hydrophobic acid (HPOA), hydrophilic acid (HPIA), hydrophobic neutral (HPON), hydrophilic base (HPIB), and hydrophobic base (HPOB). They stated that the dominant organic fractions in this water source were HPIN and HPOA and that the Trihalomethane formation potential (THMFP) obtained from these two fractions were also found to be in largest quantities when compared to other species. However, the results indicated that the most active precursors for THMFP were not the species that were present in large quantity, but were HPOB and HPIB.

They also hypothesised that the information obtained from this work could be further employed in the design of the control technique and management strategies for the water treatment plant. For example, the choice of coagulant aids might be chosen to ensure the selective removal of the target organic precursors.

Kim, H. C. and M. J. Yu (2005) investigating the structural and chemical characteristics of NOM showed that a higher formation potential of THMs resulted from hydrophobic NOM with a higher phenolic content, while haloacetic acids formation potential (HAAFP) was depended on the hydrophilic fraction They further investigated the influence of conventional water treatment and stated that the hydrophobic fraction was removed more than the hydrophilic fraction.

This improved removal of hydrophobic fractions can be explained by the different charge densities of the NOM fractions. Sharp, E. L., S. A. Parsons, et al. (2005) stated that the hydrophobic NOM fractions have a significantly higher charge density than the hydrophilic NOM fractions, whereas the hydrophilic non-adsorbed fraction has a negligible charge density. As Coagulation is believed to involve a combination of charge neutralization and complexation/precipitation, the affinity of cationic hydrolysis products for the hydrophobic fraction is greater.

However, Panyapinyopol, B., T. F. Marhaba, et al. (2005) qualified their use of coagulants to target specific NOM fractions by the fact that their work was only based on the quality of the water source during the collection period (August 2003). They stated that future work should therefore be conducted to investigate the effect of seasonal variation on the quality of organic matters and their THM formation potential.

Seasonal and catchment area variations

Scott et al., (2001) stated that during a four-year study, they observed variations in the hydrophilic content of the water ranging between 20 and 80%, with the dissolved organic matter increasing in hydrophilicity during the summer months. They hypothesized that the observed variations throughout the year could be explained in relation to microbial driven mechanisms of DOC release.

However, an investigation by Matilainen, A., N. Lindqvist, et al. (2002) into the removal of NOM (Lake Roine, Finland) at different stages of the treatment process showed that there was little seasonal variation detected in the NOM content in the raw water. They hypothesized that this was due to the fact that raw water sources in Finland are large and residence times are long, hence they do not react to seasonal variations so easily than river sources or small water systems. In their paper they also showed that high molecular weight (HMW) matter was clearly easier to remove in coagulation and clarification than low molecular weight (LMW) matter.

The proportion of each class of organic matter is greatly influenced by such factors as hydrological pathways, physical and geo-chemical characteristics of the catchment basin, temperature/sunlight and biological predominance. (Wilkinson K.J. et al., (1997)

Anderson et al (2000) investigating the nature of natural organic matter in acidified and limed surface waters, stated that differing catchment vegetation apparently effects the molecular weight distribution of the NOM in the drainage and in-lake processes. Using results from ultrafiltration, HPSEC analyses, absorbance coefficients and C: N ratios measurements, they showed that the sample from a spruce forested catchment had relatively larger amount of large molecular size compounds than the sample from a stream that drained through small bogs.

In a article by Gjessing et al., (1999) on the background and basic characteristics of original water samples and NOM isolates, they state that these differences in the nature of the NOM, which depends on where and when it is sampled, clearly demonstrate that there is a need for better international communication between NOM scientists in order to gain sufficient knowledge about this complicated and important matter.

This is exceedingly important in terms of membrane filtration to treat NOM surface waters, as a better understanding of the composition of NOM will eventually led to a improved understanding of the fouling mechanisms.

2.7 Membrane fouling

Fouling is one of the biggest obstacles to using membrane filtration in water treatment. As natural organic matter has been shown to be a major foulant in the application of membrane technology, it is very important to understand the mechanisms of interactions amongst NOM, inorganic particles and membranes.

A review of the literature into the phenomenon of ultrafiltration membrane permeability loss, due to fouling suggests that there are three potential mechanisms that are to blame **(Table 2.4)**:

- Concentration polarisation – accumulation of dissolved substances at the membrane surface
- Adsorption of dissolved substances on the membrane
- Formation of a filter cake

Concentration polarisation (CP) is when the membrane rejects a portion of the NOM, and it remains near the membrane surface, so its' concentration is higher near the surface than in bulk solution. If the solubility of the NOM is exceeded in the CP layer, the NOM may form a gel on the membrane surface, thereby increasing the hydraulic resistance across the membrane and limiting the permeate flux.

Maartens A. S. P. and Jacobs E. P., (1999) suggested that ultrafiltration concentration polarisation concentrated humic acid particles near the membrane surface to such an extend that it precipitated, and that these precipitating substances were adsorbed onto/into the membrane surface and pores and enhanced flux decline. However, Crozes G. F. et al., (1997) showed that the momentary accumulation of particulate or organic matter on the membrane surface does not necessarily lead to irreversible fouling. Crozes also demonstrated that by adjusting the operating parameters, such as backwash frequency, transmembrane pressure and flux, the effects of CP could be limited.

Table 2.4 Review of literature into fouling mechanisms of membranes

Reference	**Membrane**	**Scale**	**DOC**	**SUVA L/(mg·m)**	**pH**	**Temp °C**	**Flux L/hm2**	**NOM retention**	**Flux decline**	**Conclusions**
Bessiere Y. et al., 2005	UF Aquasource	Bench scale	9	4.7	NDG	20°C	40-160	82%	No data given (NDG)	At a given pressure there exists an associated critical filtered volume, below which fouling is reversible by rinsing whereas above this critical filtered volume a significant part of fouling is irreversible.
Kimura K. et al., 2004	Hydrophobic UF (HPO)	Pilot scale	2.4	3.8	NDG	NDG	200	75%	NDG	Polysaccharide-like constituents were found to have greater affinity for the membrane used in this study and are principal foulants.
Frimmel et al. (2004)	P00F UF (Nadir) **NF-200B (Filmtec®, Dow)**	Bench Scale & Pilot unit	19.8 mg/l	4.7	3.7	25	72 UF **39.5 NF**	86% (UF) **>95% (NF)**	NDG	Pore fouled UF membranes will approach the rejection of NF membranes

Table 2.4 Review of literature into fouling mechanisms of membranes (cont)

Reference	**Membrane**	**Scale**	**DOC**	**SUVA L/(mg·m)**	**pH**	**Temp °C**	**Flux L/hm2**	**NOM retention**	**Flux decline**	**Conclusions**
Makdissey et al. (2004)	PES - UF (Orelis)	Bench scale	2.8 – 12	2.5 – 5.1	7.0	25	760	NDG	86-68% due to colloids **37-14 % due to DOC**	Fouling due to cake layer formation
Lee N. et al. 2004	PES, Orelis (HPO UF) **YM100, Millipore Hydrophilic (HPI) UF** GVHP, Millipore (HPO MF) **GSWP, Millipore (HPI MF)**	Bench scale	2.39-8.99	2.34 -3.1	~7	25	372-122 (UF) 856-3770 (MF)	NDG	UF HPI 17-37% **UF-HPI 15-31%** MF-HPO 55-65% **MF-HPI 15-18%**	Colloid fraction showed significantly more flux decline than the hydrophobic fraction.
Guigui et al (2002)	UF (Aquasource)	Bench	5.4	NDG	NDG	20°C	120	NDG	50%	Although the floc cake causes fouling, the chemical and physical composition of the cake can affect the level of fouling
Fan L et al. 2001	GVHP, Millipore (HPO MF) **GSWP, Millipore (HPI MF)**	Pilot	3.1-9.1	2.0 - 4.3	6.7-7.4	22°C	2230-2280	NDG	20-90% Depends on MWCO of filters	The higher the aromaticity of the NOM the greater the flux decline, and the aromatics mainly resided in the hydrophobic acids fraction.

Table 2.4 Review of literature into fouling mechanisms of membranes (cont)

Reference	**Membrane**	**Scale**	**DOC mg/l**	**SUVA L/(mg·m)**	**pH**	**Temp °C**	**Flux L/hm2**	**NOM retention**	**Flux decline**	**Conclusions**
Aoustin et al (2001)	Millipore UF PLGC (10kDa) PLHK (100kDa)	Bench	12.5	NDG	7-8	20°C	46 (10 kDa) 620 (100kDa)	74–87%	58%	Hydrophobic UV absorbing molecules are responsible for irreversible pore adsorption and fouling
Cho et al (2000)	GM (1) 10PESUF40 (2) NTR7410 (3)	Bench	3.23-6.78	3.0-6.0	6.7-8.1	NDG	Varied	NDG	(1) 57-86% (2) 31-85% (3) 32-74%	Non-charged fractions were significant foulants of these negatively charged membranes
Maartens et al (1999)	Polysulphone UF	Bench	23-85	NDG	Varied	20°C	80 l/h	NDG	39 –89%	Membrane fouling can be minimised, but not prevented, by adjustment of the pH of the feed solution.
Cho et al (1998)	Millipore UF	Bench	2.84–6.8	1.16 – 5.69	NDG	NDG	172	NDG	NDG	Non-charged NOM fractions are important foulant materials for both relatively hydrophilic and hydrophobic NOM sourced waters
Crozes et al (1997)	UF hydrophilic UF hydrophobic	Pilot	1.6 – 3.6	DNG	Varied	20°C	220 HPI 125 HPO	NDG	25% HPI 65% HPO	Operating parameters can be adjusted to limit irreversible fouling

Frimmel et al. (2004) investigating UF and NF membranes showed that NF removed most of the organic matter whereas UF rejected mainly the high molecular refractory part. The NOM-removal efficiency of UF was more dependent on the water matrix. They stated that from the results it could be assumed that O-alkyl- and aliphatic structures (e.g. found in cell walls or other biomass) were dominant in the isolated fouling layers.

Lee N. et al., (2004) stated that organic colloids as well as intercellular and/or extra-cellular algal organic matter may cause significant membrane fouling and these foulants are likely to deposit a gel layer on UF membrane surfaces. Lee expanded on this with further water sources, as described in Lee N. et al.,(2005) stating that morphological analyses indicated that the surface topography of fouled UF membranes was elevated, presumably due to deposition of NOM on the membrane surface.

Makdissy et al. (2004) also showed that the most significant flux decline was due to the organic colloid fraction, a hydrophilic fraction consisting mostly of bacterial cell wall residues. Their research also showed that the colloids, which incorporate 2/3 of dissolved organic structures and 1/3 of particulate organics, exert strong fouling properties due to both rejection phenomena and the adsorption mechanism.

Maartens A. S. P. and Jacobs E. P. (1999) showed a sharp decline in the first few stages of filtration; He ascribed the sharper decline to foulant adsorption onto the membrane surface and pores. The adsorption of NOM is due to various forces, such as London-Van der Waals interaction, the electrical double layer effect and hydrodynamic attraction forces, and forms a film on the internal pore surface (Visvanathan C. and Aim R. B., 1989). Crozes G. F. and Mallevialle J. (1993) showed that the adsorption of low molecular weight molecules, smaller than the membrane pore size could lead to significant membrane irreversible fouling. Aoustin E. et al., (2001) also showed that hydrophobic UV absorbing molecules are responsible for irreversible pore adsorption and fouling.

In a paper on the fouling of polyethesulfone ultrafiltration membranes by NOM, Makdissy et al. (2004) stated that the fouling contribution by humic-like materials was dependant on their origin and nature. Polysaccharides, proteins and amino sugars largely present in humic-like structures, play an important role in UF membrane fouling, while aromaticity appears to be a secondary parameter.

However, Fan et al. (2001) showed that the higher the aromaticity of the NOM the greater the flux decline, and that the aromatics mainly resided in the hydrophobic acids fraction. Fan stated that the fouling mechanism controlling the flux decline involved the combined effects of adsorptive and colloidal fouling by the hydrophilic neutral fraction in the internal pore structure of the membrane.

Fan et al, conducting filtration tests on four fractions of NOM isolated on the basis of hydrophobicity and charge, using non-functionalised and anionic resins, revealed that the fouling potential for the three waters was: Hydrophilic neutral>hydrophobic acids>transphilic acids>hydrophilic charged.

However is should be noted that it is not only the nature of the NOM that affects fouling, there is also the charge properties of the membrane material used. Crozes G. F. et al., (1997) investigated the effect of membrane hydrophilicity and organic compound polarity on fouling and stated that hydrophobic compounds appeared to be the principle foulant material.

Cho et al. (2000) in a similar investigation, indicated that a membrane made of regenerated cellulose, the most hydrophilic of the membrane tested, displayed the highest permeability, and the lowest prowness to fouling by organic colloids. He stated that the non –charged fractions (hydrophilic and hydrophobic neutrals/bases) were found to be significant foulants for these negatively charged membranes.

Schaffer A. I. et al, (2001) showed that adsorption on membrane pores modifies the surface chemistry of the membrane and exacerbated the problem. This makes the choice of membrane material important. Nystrom M. et al., (1996) attributed the reduction in flux to electrostatic interactions between the negatively charged humic acids and the positively charged inorganic membrane, making hydrophilic membranes more suitable for the removal of NOM.

As adsorption is the principle fouling mechanism by NOM of membranes, the removal of these molecules is paramount. The use of a coagulation stage to flocculate the charged NOM out of solution will improve membrane performance. However, it is important to also remember that in dead end filtration, as the retention of coagulated flocs by ultrafiltration membranes is total, there is an accumulation of floc on the membrane surface forming a filter cake. The formation of a floc cake on the membrane also leads to flux reduction; the fouled membrane then requires back washing and if the fouling is serious, cleaning.

Although the floc cake causes fouling, the chemical and physical composition of the cake can affect the level of fouling. Guigui C. et al., (2002) conducted experiments that showed there is no major difference in the NOM content between the supernatant of a jar test and the permeate of a jar test supernatant filtered on a floc cake; they speculated that the reduction of the fouling between direct filtration of the supernatant and filtration of supernatant on a floc cake, is certainly due to the retention of the smallest flocs (preventing pore blocking) by the floc cake.

The research in this thesis expands on this theory, with regards to the changes in the physical composition of the cake, by investigating the effect of pressure on floc cake formation and the subsequent reductions, if any, in membrane fouling. An area of research that also requires more investigation is the role excess coagulant has on the short and long term fouling of an ultrafiltration membrane, especially during periods of low temperature. The role of pre-coagulation on the effects of membrane fouling is discussed in detail in the next section.

2.8 The use of pre-coagulation to improve membrane efficiency

The potential problem of UF membranes is the reduction in flow rates due to the penetration of colloidal and macromolecular material on and within the membrane. A strategy for improving membrane performance would be to combine it with a coagulation pre-treatment stage; thus colloids capable of entering the pores are coagulated to produce particles rejected by the membrane.

Coagulation is one of the most important processes in conventional treatment to produce drinking water. Iron or aluminum salts are added to remove contaminants by associating them with destabilized particles. There have been a vast number of articles on the optimum operating conditions for conventional water treatment. Conventional water treatment includes coagulation, rapid mix, slow mix, settling, and conventional filtration (Guigui *et al.* 2002). In theory, if microfiltration or ultrafiltration membranes are utilised in conjunction with coagulation, the level of NOM removal should be greatly enhanced, and the level of fouling greatly reduced. Such a combined process should produce higher quality water; reduce coagulant and chemical usage; have lower maintenance requirements; and require a significantly smaller footprint than the conventional treatment processes.

However questions remain as to the optimal coagulation conditions required for the combined process in terms of permeate quality and membrane fouling; is the impact of coagulation conditions modified according to the filtration mode and how does the combined process perform?

Table 2.5 is a selection of articles into the investigation of combining coagulation with membrane filtration.

Table 2.5 Research into combining coagulation with membrane filtration

Reference	Membrane	Scale	DOC mg l^{-1}	Coagulant	Flux Lm^2h^{-1}	Mixing Regime	Temp. °C	Back Washing	Permeate Quality	Conclusions
Kim, S. H., S. Y. Moon, et al. (2005)	Polysulphone UF	Bench	2.7-4.2	Alum	112-120	6min 150rpm 13min 30rpm 1hr settling	25°C	Yes	48-63% UV254 removal	Coagulation pretreatment extended the filtration time.
Choi, K. Y. and B. A. Dempsey (2004).	PES UF Regenerated cellulose UF	Bench	2.7	Alum	57-354	2min 60rpm 15min 20rpm	Room temp	No	88% of UV254 removal	Flocs that were produced under charge neutralization conditions produced lower hydraulic resistance
Pikkarainen, A. T., S. J. Judd, et al. (2004)	PvDF MF (Memcor)	Pilot	~20	$FeCl_3$	65	No data given (NDG)	NDG	Yes	0.3 mg l^{-1} DOC	Pre-coagulation improves product water quality by a factor of four
Jang, N. Y., Y. Watanabe, et al. (2004).	PAN UF (0.01µm)	Bench/ Pilot	2.1-3.6	PACl	290	5min-150rpm 10 min-30rpm 30 min settling	NDG	Yes	0.8 mg l^{-1} DOC	Pre-coagulation/ sedimentation improved permeate quality by 26-36% over UF alone

Table 2.5 Research into combining coagulation with membrane filtration

Reference	**Membrane**	**Scale**	**DOC mg l^{-1}**	**Coagulant**	**Flux Lm^2h^{-1}**	**Mixing Regime**	**Temp. °C**	**Back Washing**	**Permeate Quality**	**Conclusions**
Kabsch-Korbutowicz (2004)	Amicon UF Millipore UF	Bench	9.43	Alum	$4.3m^3/m^3/d$	3min rapid 30 min slow 1hr settling	NDG	No	59.9-69.1% DOC removal	The removal of organic substances strongly affected by the coagulant dose and pH of the solution.
Oh, J., S. J. Byun, et al. (2004)	Hydrophilic polyethylene, MF (0.1μm)	Pilot	2	PACl	63	In-line flash mixer (NDG)	10°C	NDG	NDG	Optimum coagulant dose led to minimum fouling
Lerch, A., S. Panglisch, et al. (2004).	UF X-Flow	Bench	7	PACl	80	1 minute rapid mix	4-30°C	NDG	NDG	Large particles transported to the dead-end of the capillary may cause clogging of the capillary
Janson, A., G. O'Toole, et al. (2004).	Zeeweed500 UF (0.04μm)	Pilot	$0.14cm^{-1}$ UV254	Alum	79	Shear rate $G = 90\text{-}100s^{-1}$ 5 minutes	NDG	Yes	$0.014cm^{-1}$ UV254	The primary cause of membrane fouling was likely organic in nature.
Kimura, K., Y. Hane, et al. (2004).	Polysulfone UF	Pilot	0.074 cm^{-1} UV254	PACl	2.1	NDG	20°C	Yes	0.023 cm^{-1} UV254	Irreversible fouling was not reduced by the pre-treatment

Table 2.5 Research into combining coagulation with membrane filtration

Reference	**Membrane**	**Scale**	**DOC mg l^{-1}**	**Coagulant**	**Flux Lm^{2}h^{-1}**	**Mixing Regime**	**Temp. °C**	**Back Washing**	**Permeate Quality**	**Conclusions**
Schaffer et al (2001)	Hydrophilic MF Regenerated cellulose UF NF	Bench	5-12.5	$FeCl_3$	MF- ~7900 UF-15-1320 NF-19-50	NDG	NDG	No	DOC removal MF 10% UF57-70% NF 74-94%	Effectiveness of pretreatment depends strongly on the organi type & solution chemistry.
Carroll, T., S. King, et al. (2000).	Polypropylene MF (0.2μm)	Bench	8	Alum	0.3s^{-1}m^{-2}bar^{-1}	NDG	NDG	NDG	46% DOC removal	Pre-coagulation improves NOM removal and reduces membrane fouling compared to microfiltration of the raw water.
Guigui, C., J. C. Rouch, et al. (2002).	Cellulosic hollow fiber UF	Bench	3.9	$FeCl_3$	120	Rapid & slow mixing (NDG)	NDG	NDG	80% DOC removal	Using coagulation before UF increases permeate quality;
Judd, S. J. and P. Hillis (2001).	Hydrophilic PES hollow-fibre MF (0.2μm)	Pilot	0.8-4.2	Ferric	110	30seconds rapid mix (230rpm)	NDG	Yes	~40-75% removal	A low coagulant dose appears to have a slightly detrimental effect on downstream microfiltration

Improvement in membrane performance with pre-coagulation

Guigui *et al.* (2002) reported that good coagulation conditions (nature of coagulant, pH and dose) generally used in a conventional coagulation/settling process should lead to good performance in terms of water quality for an in-line coagulation/UF process with dead-end filtration of river water.

This is emphasised by Kabsch-Korbutowicz M. (2005) who investigated the application of ultrafiltration integrated with alum coagulation for improved NOM removal, and showed that removal efficiencies were dependant on the pH of coagulation.

Oh, J., S. J. Byun, et al. (2004) stated that the least membrane resistance of microfiltration was shown at the coagulant dosage where the streaming potential of coagulated water was close to zero. Consequently, the optimum dosage of coagulant for the maximum efficiency of coagulation as well as the minimum fouling of the membrane could be obtained from streaming potential of the coagulated water in the microfiltration with rapid coagulation using an in-line flash mixer.

Judd S. J. and Hillis P., (2001) also showed that coagulation with downstream microfiltration offers a cost-effective means of removing natural organic matter, achieving a THMfp removal of around 80% at the optimum dose.

In terms of ultrafiltration, Kim, S. H., S. Y. Moon, et al. (2005) showed that coagulation pretreatment and membrane filtration reduced the residual level of UV254 from 0.076 cm^{-1} to 0.067 cm^{-1} without coagulation pretreatment. Coagulation improved the treated UV254 level to 0.039-0.054 cm^{-1}, which was a 19-42% improvement compared to that without coagulation pre-treatment.

Jang, N. Y., Y. Watanabe, et al. (2004) showed that direct UF membrane filtration removed only 40% of humic substances, however, the UF membrane with per-coagulation/sedimentation removed about 66-76% of humic substances. They stated that this was due to the removal of the high molecular weight humic substances and suspended particles, resulting in less irreversible cake layer formation.

Pikkarainen et al (2004) showed that a combined MF and coagulation process outperformed the filtration by microfiltration alone. The permeate DOC concentration of un-coagulated raw water was 1.3 mg l^{-1} compared with 0.3 mg l^{-1} for the PC-MF process. Pre-coagulation thus improves product water quality by a factor of four.

Irreversible fouling

However it should be noted that even with coagulation upfront of membrane filtration there is still fouling occurring. The effectiveness of the pre-treatment depends strongly on the organic type and coagulation solution chemistry (Schaffer et al 2001), and that the fouling is organic in nature (Janson, A., G. O'Toole, et al.2004).

This was highlighted by Kimura, K., et al. (2004) who showed that although pre-coagulation/sedimentation significantly mitigated membrane fouling, mainly by the reduction in reversible membrane fouling, the degree of irreversible fouling was not reduced by pre-treatment. This was because irreversible fouling caused by filtering the surface water examined in this study was mainly attributed to polysaccharide/protein like fractions of organic substances that cannot be efficiently removed by coagulation/sedimentation

Pikkarainen et al (2004) in there research stated that according to HPSEC UV254 data, neither clarification nor PC-MF were effective in removing low molecular weight UV254-absorbing organic materials. Their pilot scale tests indicated that coagulated raw water contained hydrophilic acid and hydrophilic non-acid fractions, which were partly adsorbed onto the membrane.

Carroll et al. (2000) investigated the impact of coagulation pretreatment on the MF of a low-turbidity (3.9 NTU) and high-NOM (8.0 mg DOC/L) content surface water. From the observation that coagulation pretreatment by iron or aluminum salt has been known to selectively remove hydrophobic rather than hydrophilic substances, charged rather than neutral substances, and larger-sized rather than smaller-sized substances, they concluded that small, neutral hydrophilic substances control the rate of fouling as they are the main components of the residual NOM after coagulation treatment.

It should be noted that the level of fouling by residual NOM after coagulation could also be affected by the nature of the membrane material. Jung, C. W. and L. S. Kang (2004) investigated the role of adsorption kinetics of hydrophobic and hydrophilic organics in an investigation with hydrophobic and hydrophilic membranes. They stated that applying pretreatment coagulation on the raw water significantly enhanced the permeate flux, however, regarding the effect of membrane properties on permeate flux, the rate of flux decline for the hydrophobic membrane was significantly greater than for the hydrophilic membrane, regardless of pretreatment coagulation conditions.

Coagulation regime for Nom removal

In reviewing the publications into coagulation and membrane filtration, the main difference between the articles is in the coagulation methodology, specifically the approach to the mixing regime. Kim et al (2005), Jang, N. Y., et al. (2004) and Kabsch-Korbutowicz (2004) all incorporated a period of settling into the coagulation regime. While Choi, K. Y. & B. A. Dempsey (2004) and Guigui, C., et al. (2002) used rapid mix followed by a period of slow mixing. While Judd, S. J. and P. Hillis (2001), Janson, A., et al. (2004), Lerch, A., et al. (2004) and Oh, J., et al. (2004) only used a period of rapid mixing, although the period varied from 30 seconds to 5 minutes.

The idea of using a combined coagulation membrane process against conventional clarification is process intensification, whereby the settling period can be removed and the flocculation period can be significantly reduced to the order of minutes rather than hours. This was highlighted by Judd and Hillis (2001) who indicated that flocs only require to grow to a certain critical floc size prior to challenging a microfiltration membrane. They stated that this is due to the sub micron pore size of the membrane, therefore only requiring the flocs to growth to around 2μm and can be reached with only 30 seconds of rapid mixing, as relating to NOM removal.

Although all the articles mention optimizing the coagulation regime in terms of pH, coagulant dose and mixing regime, in terms of NOM removal. The question remains as to the effect on membrane filtration if the coagulation is not optimal, specifically the role of excess coagulant dose on membrane filtration.

Incomplete coagulation and membrane efficiency

The use of a coagulation phase before an ultrafiltration membrane will improve the efficiency of the membrane at removing NOM. However, control of the coagulation regime is important as variations in coagulant levels can have a dramatic effect on membrane performance. Research on coagulation and membrane filtration has shown that when coagulation conditions are not optimal, with a low coagulant dose, the colloidal particles are still negative and hence stable. This incomplete coagulation leaves organic and inorganic material that can lead to membrane fouling. Judd S. J. and Hillis P. (2001) showed that a low coagulant dose apparently causes incomplete aggregation of colloidal particles such that internal fouling of the membrane takes place. At high coagulant dose, the particles become positive and stable again, reducing coagulation efficiency (Duan J. and Gregory J., 2003).

The point that a high coagulant dose exceeds the required amount of coagulant, for the NOM concentration, is referred to in this thesis as excess coagulant. The role played by excess coagulant on the fouling of membranes is an area of research that requires further research. Soffer Y. et al (2002) indicated that when coagulation is not optimal, small colloidal and iron species may be present which are free to affect and clog the membrane, increasing cleaning and running costs. They expanded on this theory in Soffer Y. et al., (2004), where they investigated the role of colloidal iron on the fouling of ultrafiltration membranes. They suggested that the initial fouling mechanism was pore blocking. Gabelich C. J. et al., (2002) investigating fouling of RO membranes showed that residual aluminium and iron, from alum and ferric chloride coagulation, degraded the membrane performance due to fouling.

The literature available on the role of incomplete coagulation, specifically excess coagulant, on the fouling of ultrafiltration membranes is scarce. An objective of this thesis is to explore the impact of excess coagulant in the long term fouling of UF membranes, and investigate what solutions may be found to curtail this fouling problem. This is especially relevant when taken in conjunction with the effect low temperatures have on the performance of orthokinetic coagulation.

With this in mind, although coagulation has been extensively researched, it is important to revise the basic principles of coagulation and see how they relate to the incorporation of coagulation and membrane filtration, specifically to the role temperature has on coagulation efficiency and the role of excess coagulant.

2.9 Backwash cycle and chemical cleaning

As already mentioned, the treatment by UF of waters with a high NOM concentration leads to fouling of the membrane. The flux reduction due to the accumulation of material on a membrane with a hollow fibre configuration is partially reversible by applying a counter flow, normally referred to as backwashing, which removes the majority of the accumulated matter. Following a backwash cycle, the membrane flux increases. The frequency of the backwashes is adjusted as a function of the raw water quality and typically is increased when the raw water solids load increases (Crozes et al 1997).

Membrane manufactures have developed backwash procedures specific to the membrane type and configuration. There are numerous articles on the use of backwashing and the consensus is that the frequency of the backwash cycle is more important than the length of the actual backwash. Kim et al (2005) highlighted this by showing that doubling the backwash time (from 30 s to 1 min) did not decrease the fouling rate, however by increasing the frequency of backwash from once every 15 minutes to once every 10 minutes, a backwash time of 30 s reduced the fouling rate.

Lerch et al (2004) investigating the role of temperature on the frequency of backwash cycles, showed that the backwash efficiency was highest at the highest temperature (30°C) and gets worse with decreasing temperature. This was due to the measured diameter of the floc aggregates increasing with increasing coagulation temperature, enabling them to be easier removed by backwashing.

However, no matter the efficiency of the backwash regime, membrane fouling is not totally reversible due to adsorption of NOM and small colloidal and iron species. As the number of filtration cycles increase, irreversible fouling increases. When the membrane flux decreases below acceptable levels, chemical cleaning of the membrane is required.

Regardless of the membrane system used, chemical cleaning is cumbersome and requires the shutdown of the unit being washed for several hours. As there are concerns that repeated chemical cleaning might affect the membrane life, chemical cleaning should thus be limited.

There are numerous agents available for cleaning membrane systems; they include alkaline reagents (e.g. sodium hydroxide); acidic reagents (e.g. citric and hydrochloric acids) as well as chelating agents (e.g. EDTA). However the optimal choice of cleaning agent is a function of membrane type and the level and type of fouling and is a complex matter.

This was highlighted by Lee, H. J., G. Amy, et al. (2001) who showed that foulants derived from a hydrophobic NOM source were cleaned more effectively, in terms of flux recovered, by acid and caustic cleanings compared to foulants from a relatively hydrophilic NOM source. They state that high ionic strength cleaning (with 0.1M NaCl) was more effective in promoting flux recovery for the membrane fouled with the relatively hydrophilic NOM than the other cleaning chemicals.

However Kumiura et al (2004) found that NaCl were not effective in mitigation of the irreversible fouling and that effect of chelating agent (EDTA) and acid (HCl and oxalic acid) was very limited in their study. They should that for their water an alkaline solution (NaOH) was more efficient than the chelating agent and the acid solutions in recovering membrane permeability. The oxidizing agent (NaClO) exhibited the best cleaning performance among the tested chemicals. Their results implied that some fractions of organic substances rather than inorganic ones caused the irreversible fouling.

This difference is emphasized by likkanen et al (2002) who showed in their studies that alkaline cleaners with chelatants resulted in the most efficient cleaning both in terms of flux recovery and foulant removal.

No matter the chemicals used, the research has shown that when the backwash and cleaning procedures are optimized the membrane recovers flux. The common theme amongst the articles is the fouling was due to organic fouling. Botes et al (1998) showed that if membrane was subject to cleaning every 1 to 3 weeks and the permeate backwashing was optimised to counteract the effects of concentration polarization and gel fouling they indicate that a membrane life of >5 years was possible.

The question remains as to the effect on cleaning if fouling occurs due to incomplete coagulation, specifically excess coagulant. Although in theory acidic or chelating agents should remove the inorganic material, there is very little research published on the long-term implications to cleaning regimes of excess coagulant, particularly during cold weather conditions. This thesis aims to address this issue.

2.10 Coagulation

The efficiency of coagulation for the removal of natural organic matter is variable, depending on the physical and chemical characteristics of the water to be treated. It is therefore imperative to optimise the coagulation process in terms of pH control, amount of coagulant and the mixing regime. As NOM is mostly negatively charged, and hence stable due to electrical repulsion, the addition of cationic hydrolysis products can destabilise the NOM and induce coagulation under the correct conditions of dosage and pH.

The two main coagulation mechanisms are sweep flocculation and charge neutralization. Sweep flocculation occurs when colloidal NOM and small particle are enmeshed in a growing amorphous hydroxide precipitate and effectively 'swept out' of the water (Duan J. and Gregory J., 2003). Charge neutralization occurs when the addition of hydrolysing coagulants neutralises the negative surface charge promoting coagulation.

A detailed description of the various coagulation mechanisms can be found in Cheng W. P. and Chi F. H. (2002), Gregor J. E. et al., (2002), Adachi Y., (1995) and Duan J. and Gregory J. (2003). Although the actual mode of action in coagulation is not yet fully understood, it is generally agreed that the pH of the solution determines the coagulation mechanism.

2.10.1 pH of Coagulation

pH control is one of the most important factors governing natural organic material removal (Crozes G. et al., 1993). The importance of pH derives from the fact that, the type of hydrolysis species formed is dependant on the pH of the solution when metal salts are added (Budd G. C. et al., 2004). Coagulation by the use of hydrolysed coagulants, such as alum or ferric sulphate, occurs when hydrolysed species ($AlOH^{2+}$, $FeOH^{2+}$) or solid hydroxide ($Al(OH)_3$, $Fe(OH)_3$) interact with colloidal particles.

The ferric ions can be hydrolysed and precipitated as ferric hydroxide in the pH range 3 – 10, although the predominant coagulation of adsorption and charge neutralisation occurs at pH 3 – 5, the number of hydroxide colloids tends to rise as the pH becomes more acidic (Adin A. et al., 1998). Alum on the other hand performs well in a relatively narrow pH range of 6 – 9, best at pH 6 – 7; the predominant coagulation mechanism being sweep or adsorption of micro-flocs. In the case of alum, if the pH is too low a soluble compound ($Al.OH.SO_4$) will form and if too high, the aluminium becomes complexed into soluble aluminate ions.

Lee L. D. et al., (2000) showed that the highest removal of NOM occurred at the charge neutralisation condition. He hypothesised that it may be because soluble organic species become less electro-negatively charged at the lower pH and thus subject to be easily coagulated. Soffer Y. et al., (2000) showed that coagulation at pH 5.5 could remove 56% of DOC and 35% UV254 absorbance by adsorption and charge neutralisation, but for the higher pH, where sweep flocculation prevails, the removal was only 11 % and 15% respectively.

Research has shown that the pH of coagulation and choice of coagulant is dependant on the type of water to be treated. Volk C et al., (2000) showed that at lower pH, ferric coagulants performed generally better for the removal of organic carbon than alum or poly-aluminium chloride. DOC removal data by Pikkarainen A. T. et al. (2004) revealed that ferric salts were more effective than aluminium salts in precipitating the IMW aromatic NOM fraction; and the least effective coagulant in removing this fraction was aluminium. Budd G. C. et al., (2004) and Vilgé-Ritter A. et al., (1999) also showed that ferric salts often offer a greater capability for DOC removal. Adin A. et al. (1998) shows that alum performs better than iron for turbidity removal, but worse for DOC removal.

There have been numerous studies conducted on both ferric salts and alum as coagulants and there is a wide difference of opinion as to the best coagulant. Both coagulants have advantages and disadvantages depending mainly on the water quality parameters to be treated, the main difficulty being the removal of dissolved organic matter.

2.10.2 The addition of lime for pH control

One of the problems faced in removing soluble NOM from low turbidity waters is the inability to produce an acceptable floc. Natural turbidity provides a ready source of nucleating sites for floc development, and once present these flocs act as adsorption sites for soluble NOM. For natural waters with low turbidity, these essential nucleating sites are limited, and need to be provided artificially. One solution is the addition of lime for pH control. The particulate nature of lime provides nucleating sites for floc formation and growth.

There has been various research conducted into the order of addition of coagulant and pH-adjusting chemicals. Gregor J. E. et al., (1997) conducted research into the point of addition of lime with alum as the coagulant. They found that the most useful point of addition for lime, to affect pH control of coagulation and to act as a nucleating agent, is immediately after coagulant addition; if the lime is dosed before the alum, the usefulness of lime as a nucleating agent is lost because it is substantially dissolved by the time coagulation takes place.

This thesis instead investigates the impact of lime addition with ferric sulphate as the coagulant. Of specific interest is the role lime addition has on the formation of flocs during periods of low temperature, an area of research where there is surprisingly little data in terms of the effect on membrane filtration.

2.10.3 The effect of temperature on coagulation

An area of research that has not been widely published is the effect of temperature on the coagulation process with regard to membrane filtration. Seasonal variations in temperature in the order of ~12°C can affect formation of flocs, in respect to floc density, size and growth. The only recent paper published about seasonal variations and ultrafiltration membranes was by Tiexeira M. R. and Rosa M. J. (2002), who published a report on pH adjustment for seasonal control of UF fouling by natural waters. The research conducted in Portugal highlighted the changes in turbidity throughout the season and the steps taken to improve coagulation; temperature however remained reasonably constant. With upland UK waters, the main difference throughout the seasons is temperature and this is an area I believe requires further research.

Water temperature can apparently affect fluid and particle motion, particle-particle interaction, rate and extent of hydrolysis of metal salts coagulants, and adsorption and precipitation rates (Kang L. S. and Cleasby J. L., 1995). Kang showed that a decrease in temperature from 25 to 5°C results in the lowering of the equilibrium $Fe\ (OH)_3$ at minimum solubility by 0.2 log units and shifting coagulation about 0.4 pH units to the alkaline side. Mohtadi M. F. and Rao P. N. (1973) also observed this shift of optimum coagulation pH at low temperatures, and found that increasing the pH could offset some of the adverse effects due to cold temperatures.

A shift in pH was also observed in alum at low temperatures. Edzwald J. K. (1993) showed that the pH of minimum solubility for Al shifted from pH 6.2 to pH 6.7, and that the solubility of Al decreases for the pH above 6.2 and increases below pH 6.2. Research also shows that the lowering of water temperature clearly affects the coagulant behaviour and can affect the residual aluminium leaving the plant (Dolejs P., 1992),(Budd G. C. et al., 2004).

Hurst A. M. et al., (2004) indicated that the flocs formed at low temperature are relatively smaller and that the rate of flocculation is slower. As velocity gradients decrease with temperature, due to the increase in viscosity of the water, he observed a decline in orthokinetic collision efficiency.

This is an area of research that needs further investigation, particularly the residual levels of coagulant metals, as the coagulation process is to be implemented upfront of an ultrafiltration membrane. Since low temperatures affect the orthokinetic flocculation, the role of shear rate in the mixing regime is also important.

2.10.4 The mixing regime

The role of rapid mixing has been investigated by a series of researchers over the past 30 years and can be divided into two areas of interest, the chemical or physical parameters. The chemical research involves the nature of the coagulants and their coagulation mechanisms while the physical research focuses on the effects of rapid mixing has on flocculation (Kan C. et al., 2002).

To measure the formation and growth of flocs due to rapid mixing, this research utilises the Photometric Dispersion Analyser (PDA). The PDA can monitor flowing suspensions; in particular it provides an analysis of the state of aggregation of a suspension (Gregory J., 1981). The PDA allows the analysis of flocculation at an early stage, long before the flocs are visible.

In drinking water treatment, turbulent mixing in a flocculation reactor is typically described by the average characteristic velocity gradient or shear rate, G (s^{-1}). **Eq. (1)**

$$G = \sqrt{\frac{N_p \rho N^3 D^5}{V\mu}} = \sqrt{\frac{\bar{\varepsilon}}{\nu}}, \qquad \textbf{Eq. (1)}$$

Where N_p is the impeller number, ρ is the fluid density, N is the impeller rotational speed, D is the impeller diameter, μ is the fluid dynamic viscosity, $\bar{\varepsilon}$ is the reactor average turbulent energy dissipation rate, and ν is the kinematic viscosity of the fluid. Hopkins D. C. and Ducoste J. J. (2003) showed, with alum the floc growth increased as G increased, regardless of particle concentration or coagulation mechanism, due to the greater particle collision frequency with greater shearing rates. In addition, they also showed higher particle concentration increased particle collision frequency in the reactor thereby generating greater floc growth. Moreover, greater floc growth was achieved with flocs produced with sweep floc coagulation mechanism than with the charge neutralization mechanism.

Guigui C. et al., (2002) stated that the floc structure (porosity, density and cohesion force) may differ as a function of the coagulation mechanism: the flocs formed at the lowest pH and doses are reported to be denser and less porous than those formed with sweep flocculation.

Kan C. et al., (2002) investigated the time required for rapid mixing and showed that the re-aggregation of flocs formed from charge neutralisation coagulation, results in the same or lower residual turbidity, while those formed from sweep coagulation resulted in higher residual turbidity, suggesting the break-up of micro-flocs in sweep coagulation. Spicer P.T. and Pratsinis S.E. (1996) also showed than although an increased shear rate increases the floc growth rate, the average size of the flocs decreased.

In literature there are rather contradictory recommendations for rapid mix parameters: Kan C. et al., (2002) suggested that 60 seconds of rapid mixing was adequate for the formation of micro-flocs; while Rossini M. et al., (1999) indicated that a short rapid mixing period (10 seconds) was adequate, although that was with a model kaolin solution.

Pikkarainen A. T. et al., (2004) studying the removal of DOC by coagulation before a microfiltration membrane, stated that at the shortest flocculation time studied (30 seconds), the particles had already grown sufficiently large to be removed by the membrane.

This is an area that requires further research; particularly the role of shear rate in the coagulation performance of low turbidity, high NOM waters; with regard to low temperatures and the impact the coagulation has on down stream ultrafiltration membranes.

2.10.5 In-line coagulation control

It is often the case at water treatment facilities that operators may apply high coagulant concentrations to improve treated water quality, even though the improvements in water quality may not equate to the increased operational costs. More importantly, it is possible that greater feed rates of coagulant can be detrimental to downstream processes (Dental, 1991). The use of enhanced coagulation is common practice to compensate for variations in raw water quality, as there is not an accurate and reliable dosing control method on the market. Although inline UV254 and colour monitors are in use, impurities in water, such as iron, can give false readings leading to dosing problems.

As the optimum coagulant dose corresponds to the situation where the iso-electric point is close to zero (Hlavacek M. R. J. F., 1995), (Duan J. and Gregory J., 2003), the use of zeta potential as a sensor for closed loop coagulant control is one potential solution. This research investigates the role of zeta potential in controlling coagulant dose.

The zeta potential is the parameter that determines the electrical interaction between particles, a high value prevents flocculation, reducing the value allows particles to approach each other and flocculate, the fastest rate of flocculation being the point of zero zeta potential **(Fig 2.4)**.

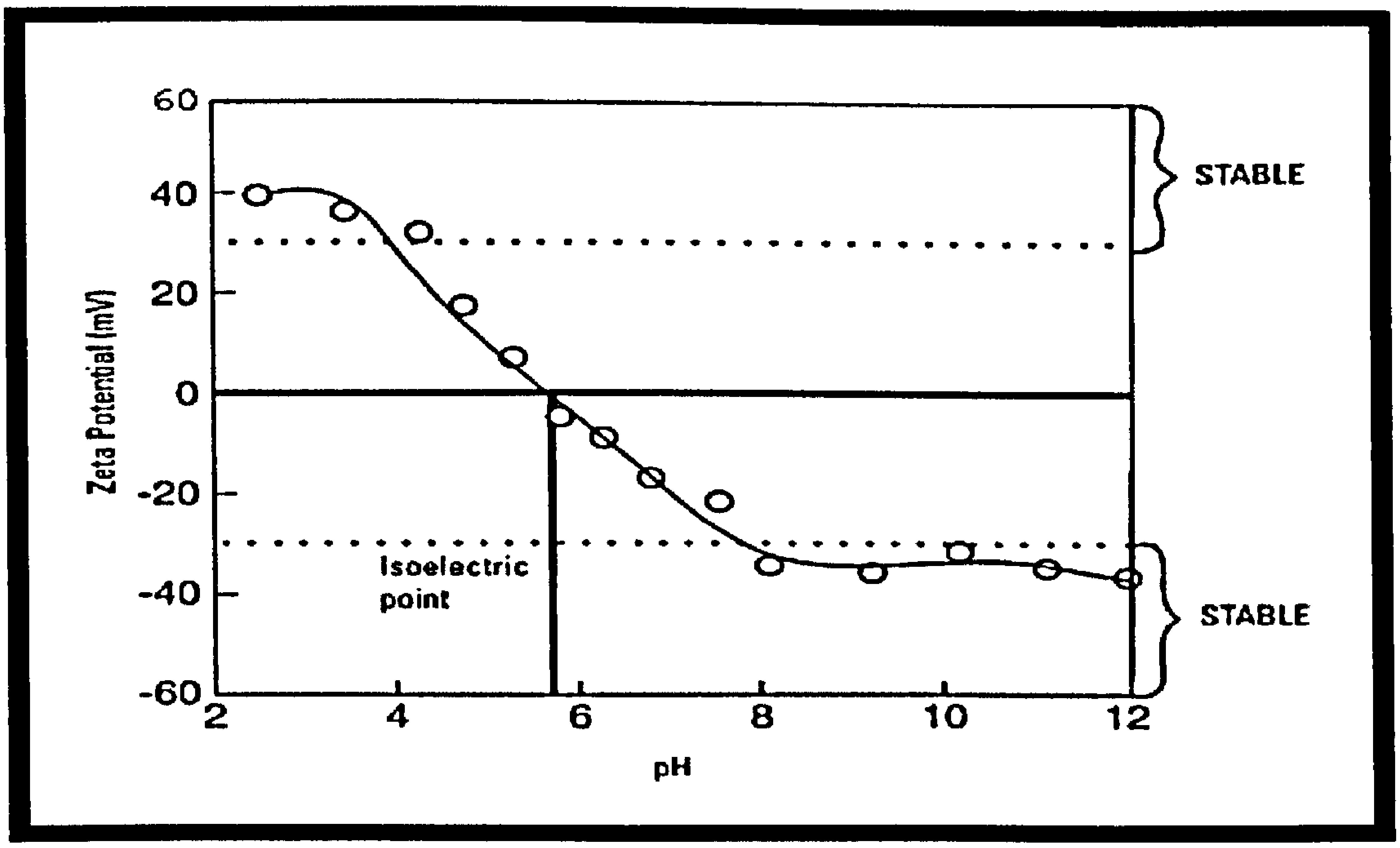


Fig 2.4 An example of changing zeta potential

The theoretical basis for the concept of zeta potential is described by the DLVO theory, explained in detail by Hunter R. J. (1998). This demonstrates how colloid stability is determined by the balance between the Van der Waals attractive forces and electrical repulsive forces (zeta potential) between particles. The natural organic matter in water is negatively charged and the addition of hydrolysing coagulants neutralises the negative surface charge promoting coagulation.

Although there are zeta potential analysers on the market, they are limited to waste water treatment due to detection limits requiring high suspended-solid concentrations. In conjunction with Malvern Instruments, this research investigates the role of zeta potential to detect changes in coagulation conditions for low turbidity, high NOM surface water.

2.11 Magnetic Ion Exchange

While ultrafiltration is considered to be a very effective technology for the removal of turbidity and bacteria, the removal of NOM can lead to fouling, even when combined with a coagulation stage, specifically in terms of low molecular weight acids and neutral NOM. An alternative treatment for low turbidity, high NOM water is the use of ion exchange resins. Bolto B. et al. (2002) showed that ion exchange resins are very proficient at removing humic substances from water supplies as a large fraction of NOM can be characterised as anionic polyelectrolytes. In a review of the influence of resin structure on performance by Bolto B. et al. (2004), he stated that a practical NOM removal process would need short contact times, and that magnetic ion exchange is attractive as the resin beads can be very small (~100 μm), so that fast reaction rates are attained.

The magnetic ion exchange (MIEX®) DOC process was developed by Orica Watercare, South Australian Water Corporation and the Commonwealth Scientific and Industrial Research Organisation (CSIRO).

The MIEX® DOC resin was designed specifically for the removal of DOC from drinking water. When in contact with water, negatively charged DOC is removed by exchanging with a chloride ion on active sites on the resin surface. This results in a reduction in the DOC level and a small increase in the treated water chloride level. In the regeneration process, resin loaded with DOC undergoes a reversed ion exchange reaction, where the resin substitutes chloride ions for DOC that is released from the resin into concentrated brine (NaCl) solution **(Fig 2.5)**.

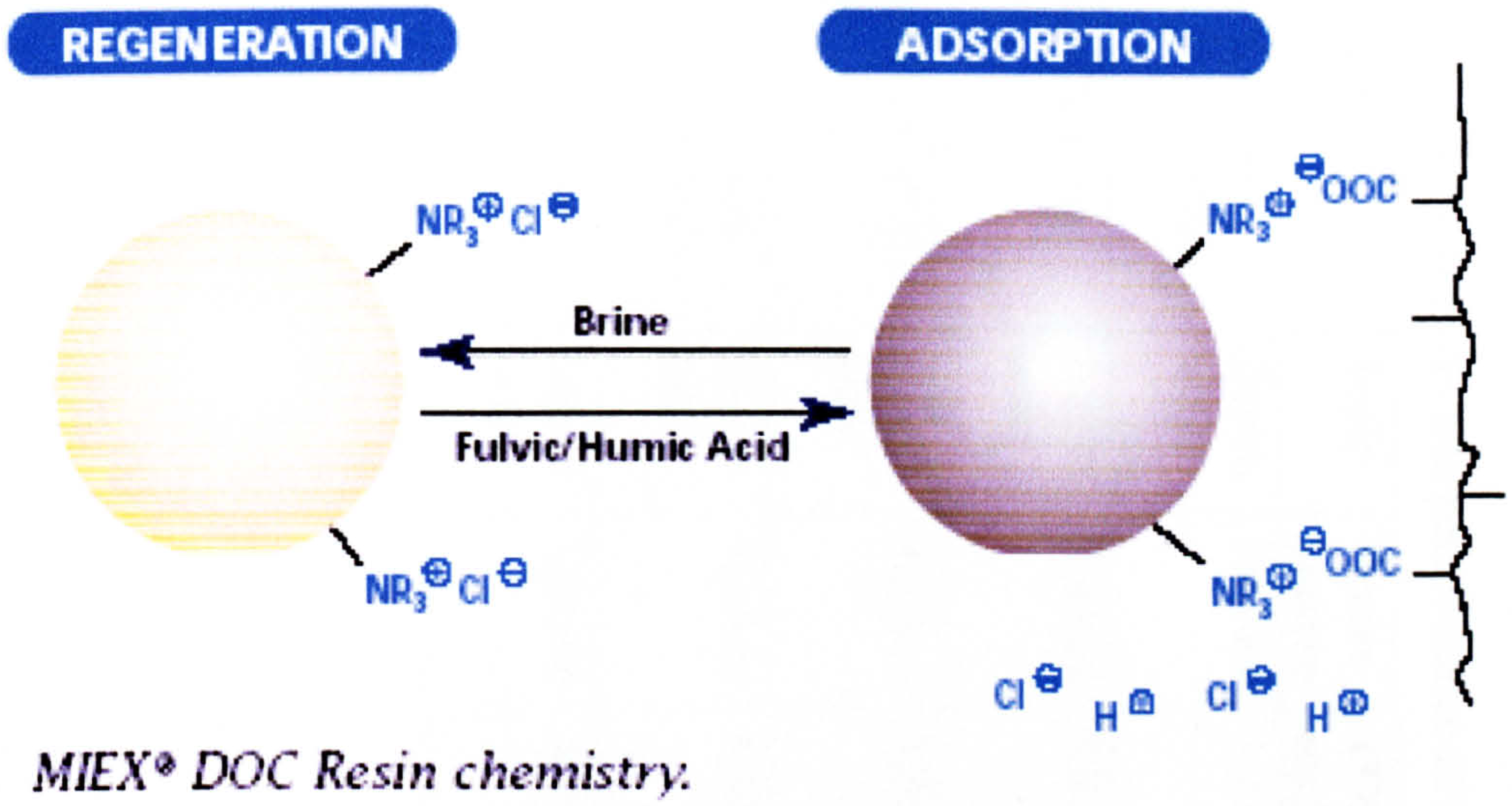


Fig 2.5 Resin Chemistry, Source: Orica Watercare

The resin has a very small particle size with a mean particle diameter of 180um. While the specific surface area is comparable to other conventional macro-porous resins, the MIEX® resin has a lot more external bead surface area. This benefits the DOC kinetics (less control by particle diffusion) and the resistance to fouling (less DOC exchanged into the particles due to shorter diffusion paths within the smaller beads)(Slunjski M. et al., 2000).

A magnetic component is built into the resin particle structure so that when mixing is removed, the fine resin beads rapidly agglomerate into larger, fast settling particles. Research conducted by ORICA show that MIEX® used in a continuous ion exchange process, is highly effective at removing low and medium weight TOC (Bourke M. et al., 2004).

There has been increased interest in the use of MIEX® by water companies looking at alternative treatment methods for reducing the DOC content of their waters. **Table 2.6** shows the parameters and performance of recent MIEX® trials that have been published.

Table 2.6 The parameters and performance of recent MIEX® trials

Reference	**Scale**	**Water Source**	**TOC mg/l**	**SUVA L/mg m**	**pH**	**Coagulant**	**DOC reduction**
Boyer T. H. and Singer P. C. (2005)	Bench scale	Surface	1.9 to 5.5	2.2 to 5.1	7.5 to 8.1	Alum	72% with MIEX
Humbert H. et al., (2005)	Bench scale	Surface	5.6 to 6.7	2.2 to 2.9	7 to 7.9	$FeCl_3$ Alum	78 % with MIEX
Fearing D. A. et al., (2004)	Bench scale	Surface	7.5 to 11.7	4.5 to 5.1	5.9 to 6.9	Ferripol	60% with MIEX 75% MIEX & Coagulation
Johnson C. J. and Singer P. C., (2004)	Bench sale	Surface	4.42 to 6.16	4.6 to 6.8	8.1		70 % with MIEX
Singer P. C. and Bilyk K., (2002)	Bench scale	Surface	2 to 8	1.4 to 4.5	6.1 to 8.1	Alum	75% with MIEX 87% MIEX & Coagulation

Johnson and Singer (2004) showed that MIEX® treatment was very effective for removing NOM. For the waters examined, the DOC concentration and UV 254 absorbance were reduced by more than 70%. They stated that since the TOC removal parallels the removal of UV-absorbing substances, this indicated that MIEX® effectively removes both the hydrophobic and hydrophilic fractions of NOM.

HPSEC/UV analysis by Humbert et al. (2005) confirmed that MIEX® was able to eliminate both high and part of low MW UV absorbing NOM, while only high MW organic molecules were preferentially removed by coagulation/ flocculation.

Boyer and Singer (2005) showed that coagulation removed 14–33% of the DOC, whereas treatment with MIEX® removed up to 72% of the DOC. They stated that treatment with MIEX® removed the HPOA, TPHA, and HPIA fractions of DOC to a greater extent than coagulation. They also stated that coagulation of MIEX treated water does not appear to remove additional DOC.

Although in their earlier work, on different water, they showed that MIEX® and coagulation reduced DOC by 87%, compared to 75% by MIEX® alone (Singer P. C. and Bilyk K., 2002). They stated that with enhanced coagulation with MIEX®, the trihalomethane (THM) and haloacetic acid (HAA) formation potential was reduced by more than 60% in all of the waters studied; reductions approaching 90% were seen in the waters with the highest specific ultraviolet absorbance values.

This improvement in DOC reduction with a combined MIEX® and coagulation process was also shown by Fearing et al (2004). Fearing showed that when MIEX® is employed on its own, approximately 60% of the DOC is removed and 70% of the UV absorbing material. When an optimum ferric dose is used, the DOC and UV removal is improved up to 75% and 90%, respectively.

Although the research was shown that MIEX® alone can reduced the DOC content between 60 and 78%, depending on the type of raw water, it is important to note that all experiments with MIEX® involved bench scale kinetic jar tests. Kinetic or contact jar tests are used to determine the dose of resin and mixing time required to reduce the NOM levels. However they do not give any indication as to the performance of the resin in a continuous process. To fully understand the relationship between batch jar tests and large-scale plants, loading jar tests and pilot scale research has to be conducted.

This thesis investigates the removal of NOM from a UK lowland reservoir with MIEX® pre-treatment upfront of dissolved air floatation. The research involves not only kinetic jar tests, but also the performance of the MIEX® resin in loading jar tests and a 30 m^3/day pilot plant. It is an area of research that would be beneficial to the UK water industry in their evaluation of MIEX® as a viable treatment option for DOC.

Chapter 3

Objectives

The aim of the thesis was to investigate hybrid clarification-filtration processes for water containing low turbidity and high levels of NOM.

This was achieved by carrying out the following objectives:

- Optimising the coagulation process for the removal of NOM and excess iron, particularly during low temperature coagulation
- Investigate the use of zeta potential to control coagulant dosing
- Assessing the impact of coagulation on membrane performance, with regard to low temperatures and excess coagulation
- If the membrane is fouled by incomplete coagulation; what are the optimum cleaning parameters
- Evaluation of the performance of MIEX ®DOC resin and dissolved air flotation in the removal of DOC from UK lowland water

Chapter 4

Experimental Techniques

4.1 Introduction

To perform the experimental measurements, water was collected from two sources: an upland reservoir feed inlet pipe at Bamford Water Treatment Works (WTW) and from the reservoir inlet feed pipe at Draycote WTW. Bamford WTW is situated in the Peak District National Park, and is fed from the Ladybower and Derwent reservoirs. The plant has a capacity of 190 Mega litres per day and provides drinking water for a majority of the East Midlands. Draycote WTW is situated south of Rugby, and is fed from Draycote reservoir. All experiments were conducted at the School of Chemical, Environmental and Mining Engineering, The University of Nottingham, except those as stated at Severn Trent Water Laboratories.

4.2 Analysis of water quality

Analysis was conducted on the water quality in the raw water and coagulated samples. The key parameters of interest were TOC; levels of iron, manganese, and aluminium; turbidity; zeta potential; particle size; and pH. With the exception of zeta potential, particle size and TOC measurements, all parameters followed the standard experimental procedures sat out in Eaton et al. (1995). The measurement procedures are set out in **Table 4.1.**

The determination of iron, manganese, and aluminium was carried out by utilising a Jenway 6405 UV/Vis spectrophotometer. Turbidity measurements were carried out using a Jenway 6035 Turbidimeter. The pH of the samples was measured by a WTW 235 pH meter. Zeta potential measurements were carried out by a Malvern Zeta Sizer 3000HS. A Shimadzu TOC-5000A analyser was used to measure TOC. The levels of NOM were analysed by multiple wavelength absorption detection. Some organic compounds in water absorb UV light at 254nm and 260nm. These compounds include humic substances, aromatic compounds and hydrocarbons.

Table 4.1. Parameter measurement procedures

Parameter	**Method number**	**Method type**	**Reference**
TOC	5310 B	High Temperature Combustion method	Shimadzu
UV_{254} & UV_{260}	5910 B	Ultraviolet Absorption method	Standard methods⁽¹⁾
Total iron	3500-Fe B	Phenanthroline method	Standard methods⁽¹⁾
Aluminium	3500-Al D	Eriochrome Cyanine R method	Standard methods⁽¹⁾
Manganese	3500-Mn B	Persulfate method	Standard methods⁽¹⁾
Turbidity	2130 B	Nephelometric NTU method	Standard methods⁽¹⁾
Zeta potential		Doppler laser scattering method	Malvern Instruments
pH	4500-H^+ B	Electrometric method	Standard methods⁽¹⁾
Chlorine Demand	4500-Cl G	Colourmetric method	Standard methods⁽¹⁾

(1) Eaton, A.D., Clesceri, L.S., and Greenberg, A.E., 1995. *Standard methods for the examination of water and wastewater.* Edited, 19th edition.

Following methods described by Eaton et al. (1995) stock solutions of aluminium, manganese, and iron were made. Using known concentration of solution, the absorption readings were recorded and calibration curves were calculated. The calibration curves for all spectrophotometer experiments are shown in **Appendix D.**

A summary of the major test apparatus and analytical instruments used for the investigation, including the measured parameters, range, model number, and manufacturers are listed in **Table 4.2.**

Table 4.2: Specifications of major instruments

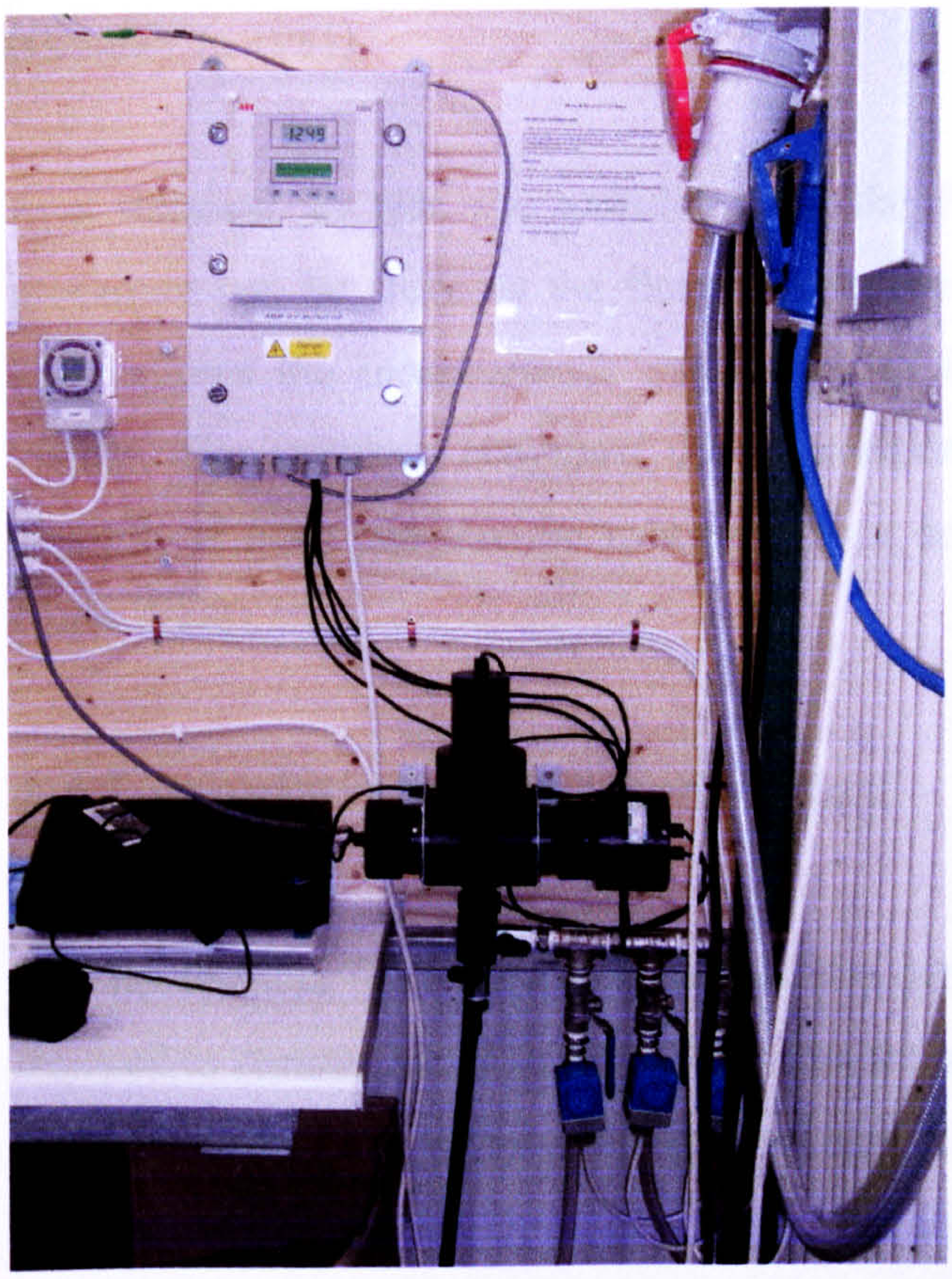
Apparatus/ Instrument	Measurement Parameter	Measurement Range	Model No.	Manufacturer
Zeta Sizer	Zeta Potential	0.1 – 200 mV	3000HS	Malvern Instruments Malvern, UK
Zeta Sizer	Particle size	0.1 - 5000μm	3000HS	Malvern Instruments Malvern, UK
pH meter	pH	1-14	235	WTW®
TOC Analyser	TOC	50 ppb to 4,000 ppm	TOC-5000A	Shimadzu, UK
Stirrer	Jar test	25 to 250 rpm	Stuart SW6 Flocculator	Bibby Sterlin Ltd Stone, UK
Photometric Dispersion analyser	Floc growth	0 to 3 Ratio units	PDA2000	Rank Brothers Ltd Bottisham, UK
Turbidity meter	Turbidity	0-199.9 NTU	6035	Jenway Limited Dunmow, UK
Pump	Flow rate	0 to1000 l/min 2.2μl/min to 37ml/min	Masterflex 7550 Masterflex 77120	Cole-Palmer Instrument Co. Barrington, IL, USA

The analysis of the Bamford water quality was conducted at the School of Chemical, Environmental and Mining Engineering, at the University of Nottingham (additional analysis was conducted by Severn Trent Water where stated).

The analysis of Draycote water was conducted on-site at Draycote WTW using Severn Trent Water equipment. The online UV measurements were obtained using a series 7300 ABB online monitor (**Fig 4.1**). Analysis of the total amounts of aluminium, manganese, as well as total organic content (TOC), dissolved organic content (DOC) and particulate organic content (POC) were conducted by Severn Trent Water

Laboratories. TOC characterisation was conducted by DOC LABOR Germany (*Method: Liquid Chromatography – Organic Carbon detection (LC-OCD), Calibration on basis of "Suwannee River" Standard IHSS-FA und IHSS-HA).*

Figure 4.1 ABB online UV monitor



4.3 Photometric Dispersion Analyser

This work utilised the Photometric Dispersion Analyser (PDA). The PDA can monitor flowing suspensions; in particular, it provides an analysis of the state of aggregation of a suspension. The PDA illuminates the particles in the suspension by a narrow beam of light. The fluctuations in the intensity of transmitted light are monitored by a sensitive photodiode and the readings converted to voltage. From the root mean square (rms), amplitude of the fluctuating (ac) signal, and the mean transmitted light intensity (dc), the state of aggregation in the suspension can be quantified by the ratio of rms to dc, Eq. (1) (Kan et al. 2002).

$$Ratio = \frac{rms}{dc} \qquad \text{Eq.1}$$

This ratio has been shown to be a sensitive indicator of the state of aggregation (Gregory J., 1981)

In a standard jar test, the turbidity after the flocs have settled is determined. This procedure can be slow, as the flocs require time to grow large enough to settle. The PDA allows the instantaneous monitoring of flocculation long before the flocs are visible. The optimum coagulant dose corresponds to the maximum ratio value. The strength of flocs can also be measured by a decrease in ratio at higher stirring rates (Rank 2002).

4.4 Coagulation – Standard jar test

The Jar test has been used as a method for determining the optimum coagulant dose required to remove NOM in water treatment for many decades.

In the jar tests, water samples of equal volume (1000ml) were poured into a series of six 1-litre beakers on a multiple stirrer machine equipped with a programmable, variable speed drive. After the fixed coagulant dose and pH correction dose had been added to the beakers, the contents were rapidly stirred to simulate flash mixing and then the speed was reduced to simulate flocculation. After a given period of time, the mixing was stopped to allow the formed flocs to settle.

The controlling parameters were:

1. The volume of the sample.
2. The size and shape of the container.
3. Peripheral speed and time of rapid mixing and slow mixing.
4. Type and dosage of coagulant.

Coagulation and flocculation tests were conducted using a six-paddle Stuart Flocculator SW6. The coagulants used included alum, ferric chloride and ferric sulphate. The dose ranged from 0 - 6 mg/l. The ferric sulphate was provided by Severn Trent and was the coagulant utilised in their clarifiers. The ferric chloride and alum were from Sigma-Aldrich Co Ltd, Poole UK.

The standard jar test procedure included the following steps:

1. The sample water was measured for turbidity and pH value.
2. 1000ml of the water sample was poured into the 1litre jar-test beaker.
3. Controlled amounts of coagulant were added to the sample.
4. Adjustment of pH was conducted using drop-wise addition of dilute sulphuric acid or calcium hydroxide.
5. The rapid mixing was set for 1 minute at speeds of 150 – 200 rpm.
6. The slow mixing was set for 10 minutes at speeds of 30 -60 rpm.
7. After flocculation the sample was allowed to settle for 20 minutes.
8. The supernatant was collected and measured for turbidity and UV254.

4.4.1 Optimum pH and dosage

To discover the optimum coagulation regime, standard jar-test procedures were first followed to compare with published work. The optimum pH value was determined by having a fixed coagulant dose while varying the pH. The optimum coagulant dose was determined using this pH value while varying the coagulant.

The second part of the investigation utilised the Photometric Dispersion Analyser (PDA), with the optimum pH and coagulant dose being those values which increased the ratio value to the highest level and at the quickest rate. The mixing conditions for these experiments were 20 seconds with no mixing to establish a base line, then constant rapid mixing at 250rpm ($G = 447\ s^{-1}$) for 480 seconds.

4.4.2 Optimum mixing regime

The experiments to investigate the mixing regime involved rapid mixing and slow mixing. The rapid mixing experiments were as described above. The slow mixing regime involved 20 seconds with no mixing to establish a base line, then 60 seconds of rapid mixing followed by 420 seconds of slow mixing. The various shear rates for the different mixer paddle speeds are shown in **Table 4.3**. All mixing regimes are described in rpm.

Table 4.3 Calculated shear rate values for various rpm speeds.

RPM	250 rpm	225 rpm	200 rpm	150 rpm	50 rpm	30 rpm
Shear rate ($G = s^{-1}$)	447	384	321	209	39.9	19

To examine the changes in water during the mixing period, samples were collected periodically throughout the experiment and then filtered through Whatman 2 filter paper (pore size 8 µm) to remove flocs. The filtered sample was then tested for UV-254 abs. and total iron.

4.4.3 Optimum temperature

The experiments on temperature effects, involved samples of raw water being cooled to various temperatures before the experiment started. The temperature was continuously monitored, with ice packs used to maintain a steady value throughout the experiment. Room temperature experiments were maintained due to setting the thermostatic air conditioning to 20°C.

4.4.4 Optimum lime addition

The experiments on determining when to add lime comprised of: adding lime before adding the coagulant; adding coagulant and then the lime; and finally adding the coagulant and lime together. The time of addition of the chemicals is shown in **Table 4.4**. The experiments involved both rapid and slow mixing. The rapid mixing experiments used 250 rpm, while the slow mix experiments involved rapid mixing (250 rpm) for a further 60 seconds after the addition of the second chemical and then a period of slow mixing (30rpm).

Table 4.4 The time at which lime and coagulant were added.

Time	0 seconds	20 seconds	40 seconds
Experiment 1	Raw water	Lime addition	Coagulant addition
Experiment 2	Raw water	Coagulant addition	Lime addition
Experiment 3	Raw water	Lime and coagulant together	

4.4.5 Zeta potential experiments

The zeta potential experiments were conducted using a Malvern Zeta Sizer 3000HS. The experiments involved adding a known coagulant dose to a litre of raw water and gently mixing for 10 seconds to disperse the coagulant. A syringe was used to collect a 10ml sample that was then injected into the Malvern instrument. The zeta potential of the raw water sample was noted, along with the zeta potential results for the various coagulant levels.

To examine the changes during the mixing period, samples were collected periodically throughout the experiment and then filtered through Whatman 2 filter paper (pore size 8 μm) to remove flocs. The filtered sample was then tested for UV-254, TOC and total iron.

4.5 Ultrafiltration membrane experiments

For the membrane experiments with pre-coagulation, an in-line mixer was designed and built by the technicians, at SChEME, the University of Nottingham, to provide continuity with the jar test performance results. Scaled mixer vessels were built to replicate the residence time of the jar test vessels; this, combined with scaled mixing impellers, gave a calculated mixing regime which achieved the same mixing time and shear rate as the jar test results (**Fig 4.2**). 1 minute of rapid mixing is followed by variations in slow mix retention time (via control valves). Two rapid mixing vessels were used to achieve a more precise shear rate.

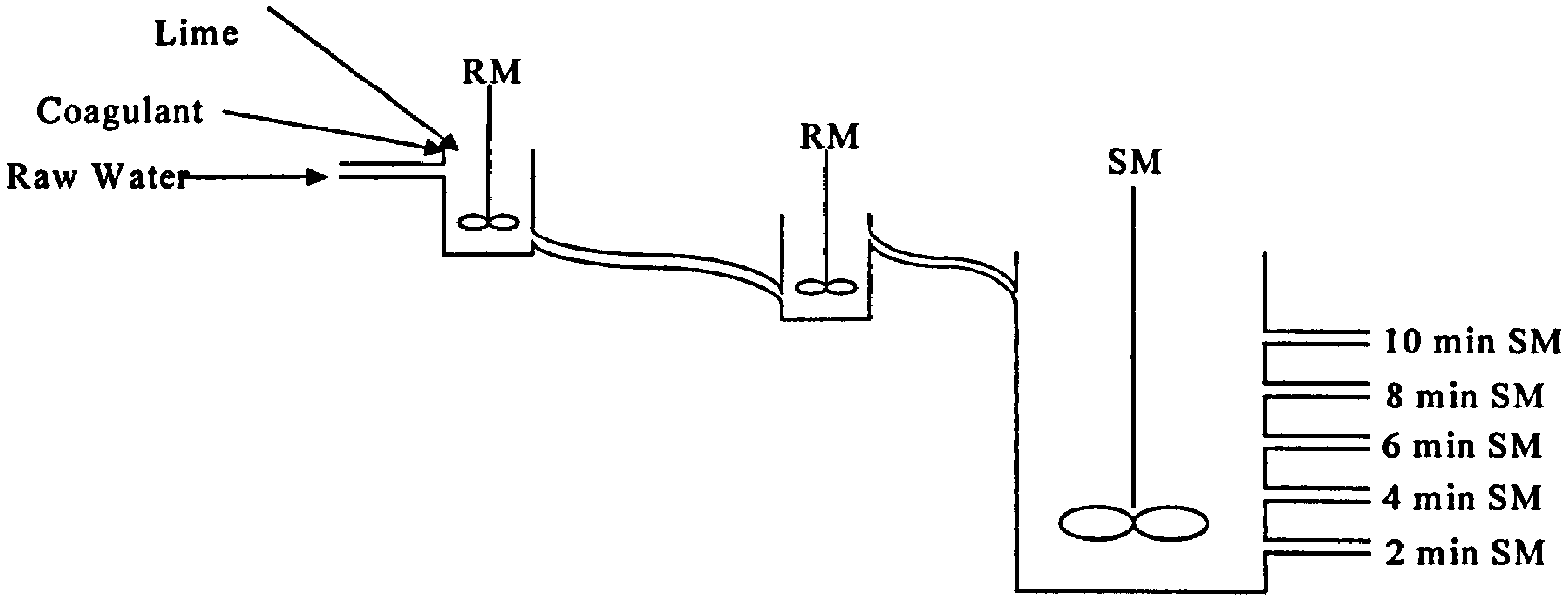


Fig 4.2 Schematic of the mixing regime

To evaluate the effectiveness of pre-coagulation upfront of a membrane system, two different membrane configurations were used. Firstly a Norit membrane was used to evaluate the effect of coagulation on a capillary membrane system. Secondly, a Zenon submerged membrane was used to determine the effect of coagulation on a hollow fibre membrane.

4.5.1 Norit Membrane (T/RX-300)

A bench scale Norit X-flow (T/RX-300) ultrafiltration membrane was used to conduct experiments on a capillary membrane system, operated in a dead-end configuration with a tube side feed. The X-flow is a polyethersulfone /polyvinylpyrrolidone blend hollow fibre membrane (PES/PVP membrane) with a nominal pore size of 0.04μm, a 0.7 mm inner capillary diameter, 150 kDa Molecular Weight Cut Off and a surface area of 3.6 m^2. The X-flow was chosen as it is hydrophilic in nature and is tolerant of a wide range of pH (1-13) allowing flexibility in cleaning.

An operating system was designed and built around the X-flow module to allow the incorporation of a pre-coagulation treatment phase (**Fig. 4.3**). Coagulated water, after the mixing process, was pumped by the unit through the membrane. The flux was set at 130 lm^2h^{-1}. The difference in inlet and outlet pressure corresponded to the transmembrane pressure. Analysis of the permeate was conducted to calculate flow rate, UV254 abs. and total iron.

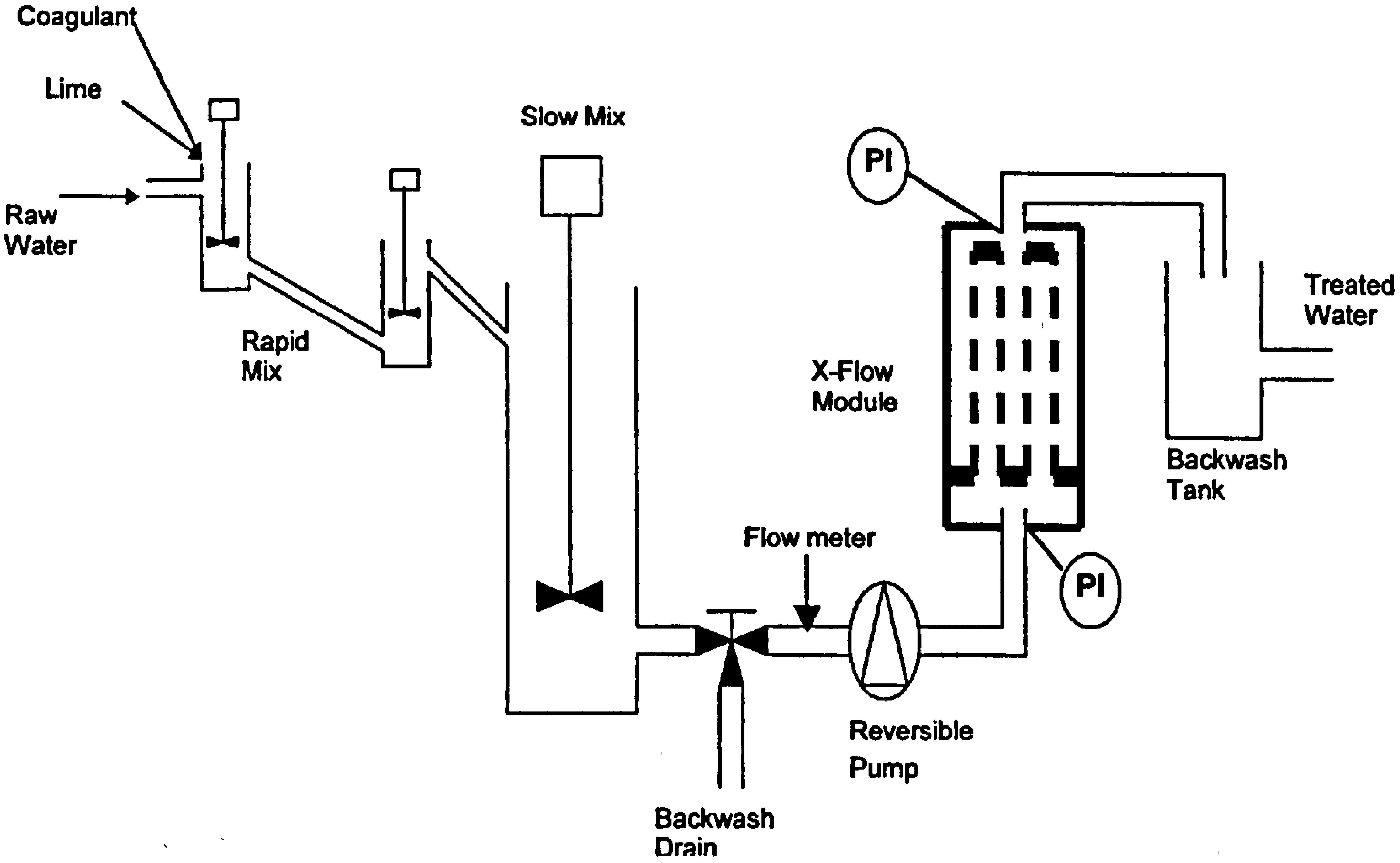


Fig. 4.3: Schematic of the Norit X-flow operating system.

The membrane unit was backwashed after each run by distilled water. The permeate flows back through the membrane, lifts off the cake and flushes it out of the module. Periodic chemical cleaning was conducted by alternatively soaking the membrane with 1% sodium hydroxide followed by 1% citric acid solution to remove organic and inorganic foulants.

To investigate the optimum cleaning regime, the raw water treated with 3 mg/l coagulant was run through the membrane with backwash cycles until the flow rate decreased to 300 ml/min. The membrane was then soaked in cleaning solutions for 2 hours before rinsing. Distilled water was then run through the membrane to measure a recovery rate. The cleaning chemicals used in this study included sodium hydroxide, hydrochloric acid and citric acid.

Scanning electron microscope analysis was conducted at SChEME, the University of Nottingham. Individual membrane fibres were analysed before and after chemical cleaning to ascertain the fouling mechanism. The fibres were dissected along a longitudinal axis to allow access to the active membrane surface (**Fig. 4.4**).

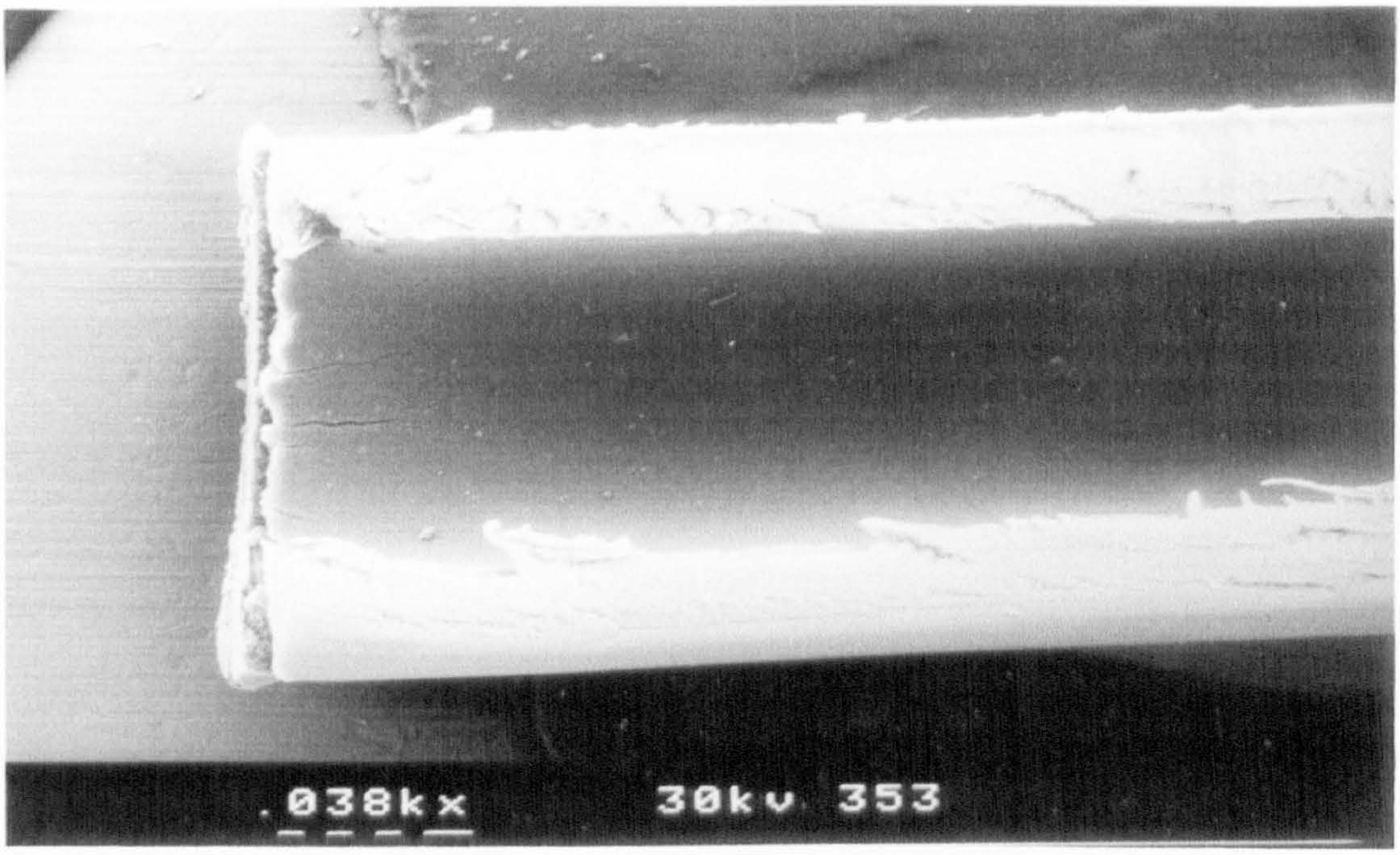


Fig. 4.4 A membrane fibre prepared for SEM analysis

4.5.2 Zenon membrane

To investigate an alternative membrane configuration, a Zenon ZeeWeed® (ZW) ultrafiltration membrane was chosen. The ZW is a submerged hollow fibre membrane which has a shell-side feed. The work involved a bench scale membrane unit (ZW – 1) and a lab scale membrane unit (ZW – 10). Experimental rigs had to be designed and built to incorporate the operation of the ZW -1 and ZW – 10. **Fig 4.5** shows a schematic of the ZW – 10 with a coagulant dosing and mixing regime incorporated into the process. The main difference in the ZW -1 design is in the size of holding tank and flow rates involved.

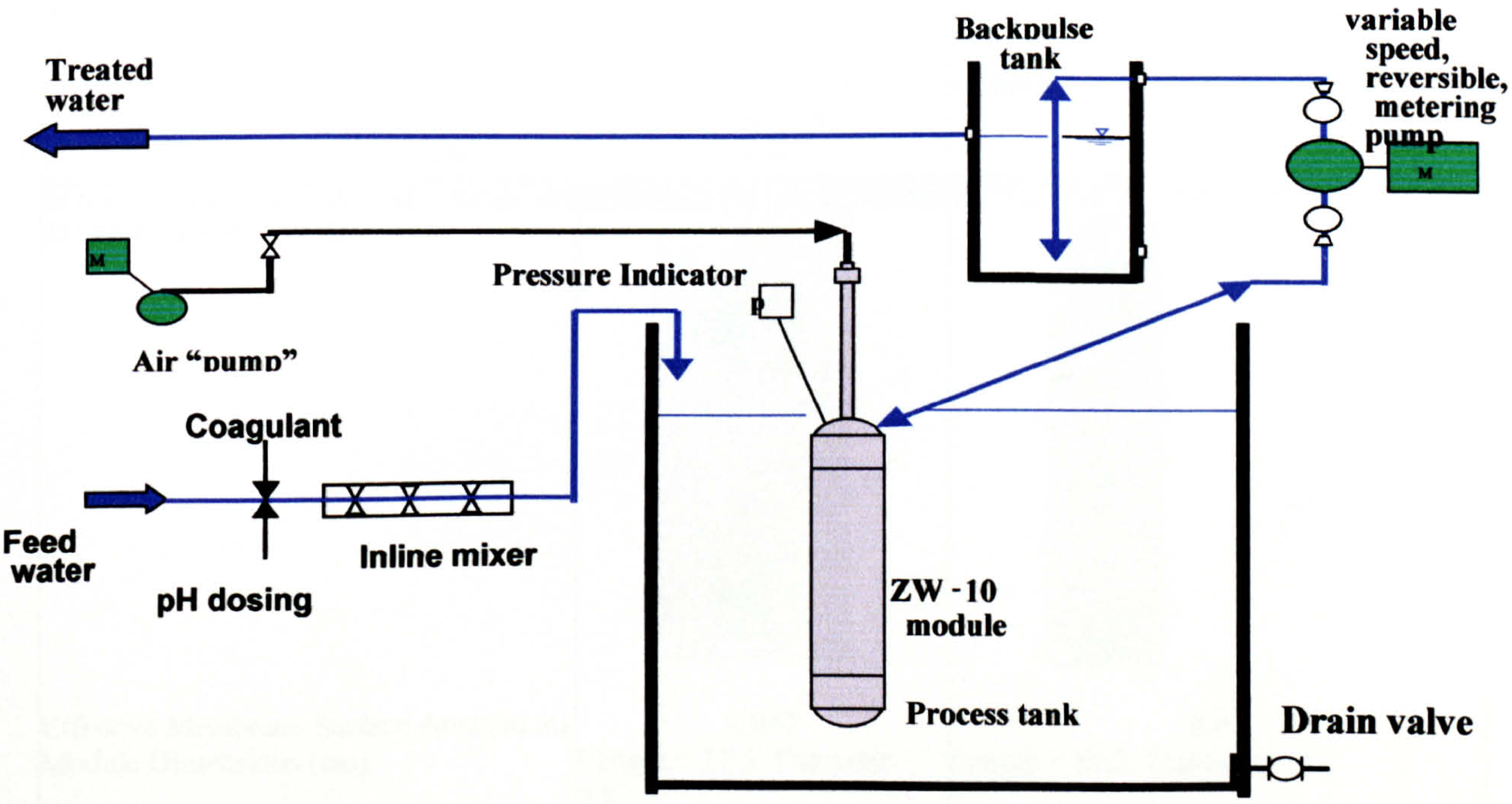
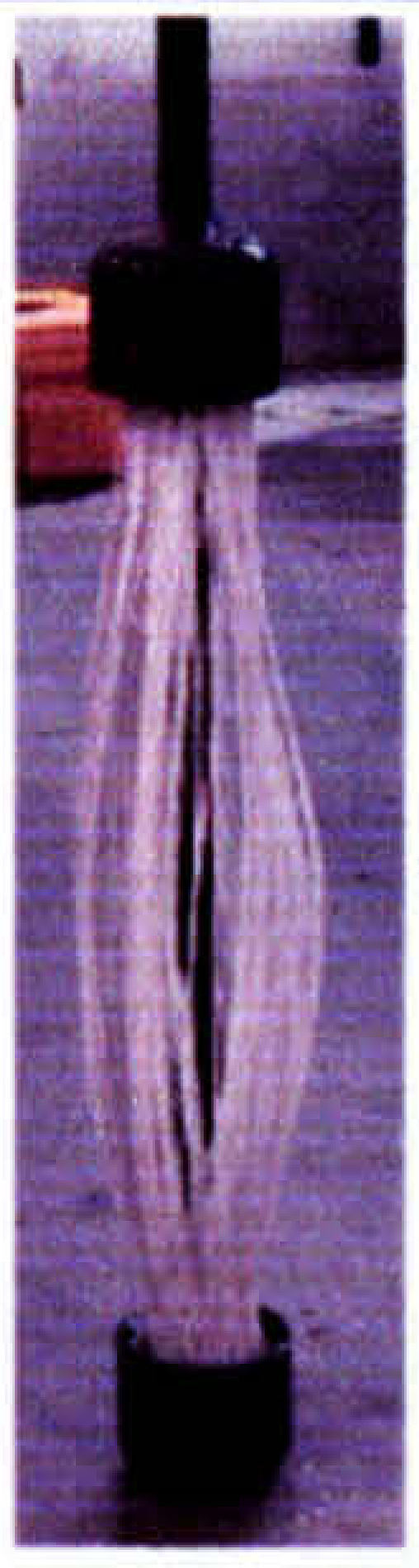


Fig 4.5 Schematic of ZW-10 membrane plant

Both membrane modules utilize the same membranes as the full scale ZeeWeed®- 500 modules and can be used to evaluate membrane fouling as well as cleaning regimes. The main operating parameters and membrane characteristics are shown in **Fig 4.6.**

Fig 4.6. Comparison between the ZW - 1 and ZW – 10 membrane units

General Description	**Zenon ZW-1 Module** Compact, inexpensive, flexible, manual bench top system to investigate effect of ZW filtration on water quality and perform fouling/cleaning studies in water and wastewater applications.	**Zenon ZW-10 System** Small, flexible, automated frame-mounted system for water and wastewater process feasibility and fouling and cleaning studies. Flux data provides good guidance for full scale system performance but can't be used for system design.
System Characteristics		
System Process Flow (L/day)	20 to 100	400 to 2000
Process Tank Volume (L)	2 to 20	190
Backwash Tank Volume (L)	1 to 2 (optional)	15
Membrane Characteristics		
Outside Diameter (mm)	2	2
General Type	supported , non-ionic, hydrophilic	supported , non-ionic, hydrophilic
Nominal Pore Diameter (micro m)	0.04	0.04
Module Characteristics		
Effective Membrane Surface Area (sq m)	0.047	0.93
Module Dimensions (cm)	Length = 17.5. Diameter = 5.8	Length = 69.2. Diameter = 11
Hold-up Volume (mL)	10	130
System Operation		
Backwash	Yes	Yes
Maximum Permeation Pressure (bar)	0.6	0.6
Operating Transmembrane Pressure (bar)	0.07 to 0.55	0.07 to 0.55
Permeate Flow Range (mL/min)	5 to 25	300 to 1200
Typical Permeate Flow (mL/min)	50	700
Maximum Backwash Pressure (bar)	0.7	0.7
Maximum Cleaning Temperature (deg C)	40	40
Operating pH Range	5 to 9	5 to 9
Cleaning pH Range	2 to 10.5	2 to 10.5
Maximum OCl- Concentration (ppm)	1000	1000

Experiments were conducted with different coagulation regimes, and the change in Trans Membrane Pressure (TMP) recorded. Periodic back-washing was incorporated to remove flocs from the membrane surface, with the improvements in TMP used to calculate the recovery of the membrane from reversible fouling.

Irreversible fouling required the membrane to undergo a cleaning regime. If there was an excessive solid build up or the process TMP exceeded 9 psi, the module was removed from the process and soaked in a tank. The general cleaning protocol involved removing any floc cake by hand, or with a gentle spray over a drain and then soaking the membrane in a 200 ppm NaOCl solution at room temperature for a minimum of 4 hours. For heavy fouling involving inorganic material, the membrane would also be rinsed thoroughly with an additional soak in citric acid (5 mg/L) solution for a minimum of 5 hours. The module was rinsed well with clean water between and after each step.

A more in-depth cleaning study was conducted with the ZW-10. The membrane was run with 2 minutes of slow mixing with periodic backwash until the TMP reached -9 psi. The cleaning regime involved soaking the module in various solutions for 4 hours and then recording the TMP reading with distilled water to discover the recovery. Cleaning solutions were sodium hypochlorite, hydrochloric acid, EDTA and sodium biosulphate. The experiment was run at various temperatures (4°C, 18°C and 35°C). The 4°C was maintained with the application of an ice pack. This was to determine if it was possible to clean the membrane using temperatures normally associated with ambient temperature during the winter period and without heating. 18°C was chosen to simulate the temperature of water found during the summer months. 35°C was chosen to discover if heating had a positive effect. Due to the makeup of the membrane, a higher temperature than this would lead to a break down in the membrane integrity. 35°C was maintained by a water bath.

4.6 Magnetic Ion Exchange

Severn Trent Water (STW) is investigating treatment process options aimed at more efficient removal of NOM from surface water sources at several of their plants. As part of those activities, STW and ORICA Watercare Europe (OWE) have agreed to conduct a trial at the Draycote WTW to evaluate the efficiency of NOM removal with MIEX®DOC pre-treatment and a downstream coagulation/DAF process. In this trial, the MIEX process will be applied to raw water prior to any other treatment. The downstream treatment will be evaluated using a pilot DAF unit (discussed in **4.7**)

A 30 m^3/day (1.25 m^3/hour) automated, mobile MIEX plant was provided by OWE, with day to day tasks and sample measurements conducted by myself and Katie Shorrock (Severn Trent) with operational aid provided by Elizabeth Martin (Orica).

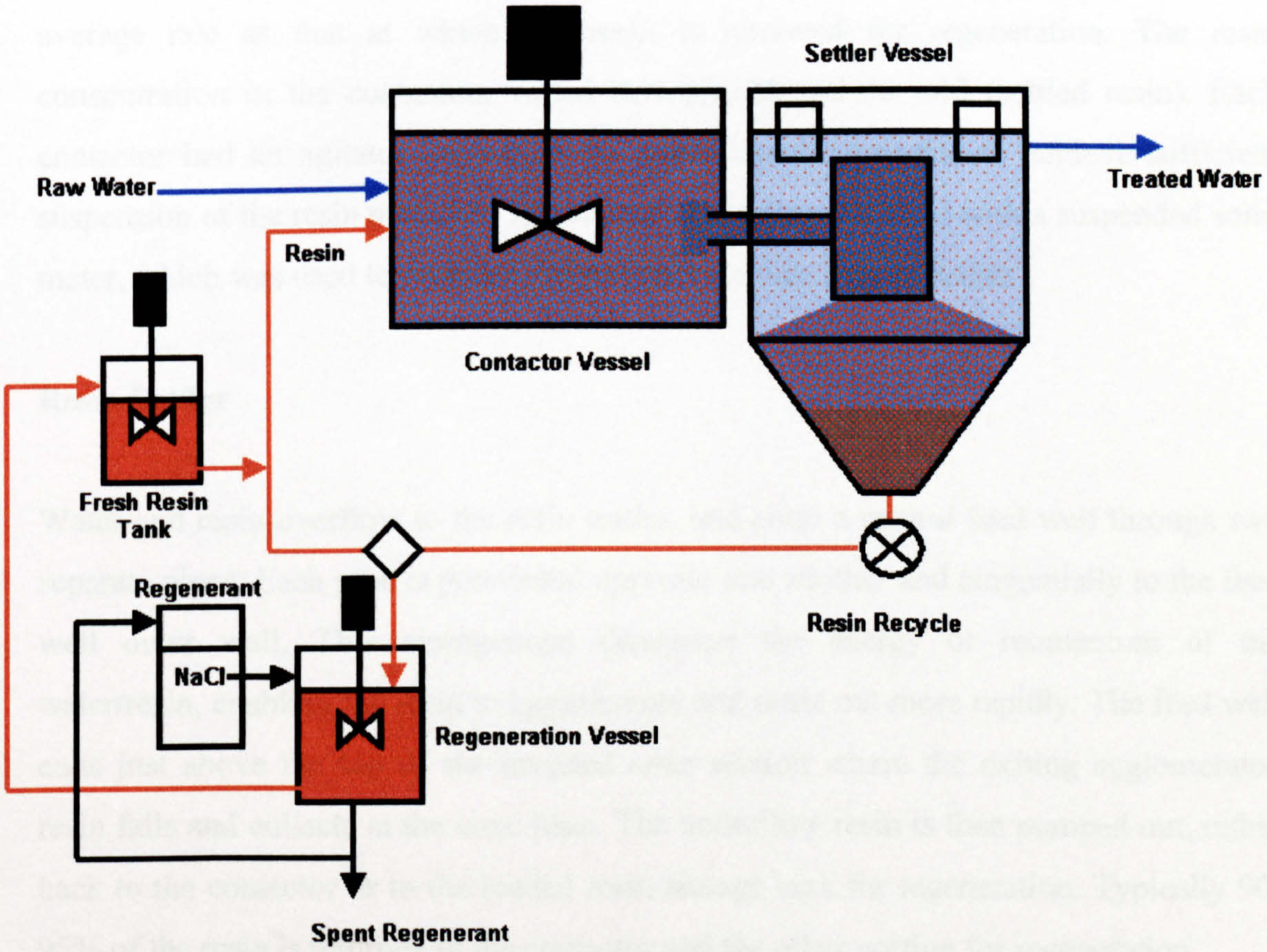


Fig 4.7 schematic of the MIEX process

The MIEX®DOC resin is utilised in a continuous ion exchange process. The resin has been developed to enable the removal of DOC from NOM laden waters.

Raw water supply

The raw water is supplied to the plant using a pressurised header supply (part of the existing site utilities). The raw water is first passed through a strainer to remove any small debris, and the flow rate is regulated by a flow meter and control valve to maintain a constant flow.

Contactors

The raw water was directed into the first of two connected contactors allowing a contact time of 10 minutes. The fresh resin is continually dosed into the contactors at the same average rate as that at which the resin is removed for regeneration. The resin concentration in the contactors varied between 20 and 30 ml/l (settled resin). Each contactor had an agitator for which the speed can be adjusted to achieve sufficient suspension of the resin particles. The second contactor was fitted with a suspended solid meter, which was used to measure the suspended solids concentration.

Resin Settler

Water and resin overflow to the resin settler, and enter a central feed well through two separate pipes. Each pipe is positioned opposite one another and tangentially to the feed well outer wall. This arrangement dissipates the energy or momentum of the water/resin, enabling the resin to agglomerate and settle out more rapidly. The feed well ends just above the top of the inverted cone section where the exiting agglomerated resin falls and collects at the cone base. The underflow resin is then pumped out, either back to the contactor or to the loaded resin storage tank for regeneration. Typically 90-95% of the resin is returned to the contactor and the other portion for regeneration.

Fresh resin supply

Regenerated resin and virgin makeup resin are stored in the Fresh Resin tank, the concentration of which is usually 200 ml/l (settled resin). The fresh resin pump doses resin to the contactor at the same average rate that is sent for regeneration.

Loaded resin tank

Resin from the recycle flow that is sent for regeneration is stored in the loaded resin tank until the previous regeneration is complete and the regeneration tank is empty. The resin is then transferred to the regeneration tank.

Regeneration tank

Loaded resin is regenerated with a brine (NaCl) solution in this tank. The general steps involved for one regeneration step are as follows:

- Accumulation of resin in the regeneration tank
- Dewatering of the regeneration tank, leaving settled resin
- Addition of brine from the brine tank
- Mixing (regeneration) of the brine-resin mixture
- Draining of brine from regeneration tank back to brine tank if brine reuse is used, otherwise brine is sent to drain
- Water washing of resin content in the regeneration tank
- Draining of rinse water to waste
- Re-suspension of resin in water to required concentration
- Transfer of suspended resin to the fresh resin tank

Brine tanks

Solid salt pellets are added to the saturated brine tank. The solids dissolve, giving a saturated brine solution of approximately 300 g/L. For each regeneration, a volume of saturated brine is pumped into the brine tank, where water is further added to achieve a diluted brine concentration of approximately 120 g/l. This solution is then pumped to the regeneration tank to regenerate the resin.

The operating parameters for the start of the MIEX trial are listed in **Table 34.5**.

Table 4.5 MIEX operating parameters.

System operations	**Parameters**
Throughput	30 m^3/day = 1250L/h = 20.83 l/min = 0.347 l/sec
Resin concentration	20 ml settled resin per L water
Contact time	10 minutes (this will be achieved by using the small set of contactors, each providing 5 min retention time)
Regeneration rate	Every 6 hours; this will be followed by a period of using 3 hours for comparison of performance
Regeneration concentration	120 g/l NaCl
Regenerant re-use (bed volumes)	3 bed volumes (1 litre of resin = 3 litre of brine
Regenerant re-use (number of times)	YES / 5 TIMES
Resin rinsing	Yes/ no; initially resin will be rinsed after every regeneration; this will be followed by a period of no rinsing for comparison of performance
Regenerant adjustment	25% salt used for fresh regenerant preparation for each use
Saturated brine concentration	325 g/l NaCl; solution only to be used in saturated brine tank.

Raw water and MIEX treated samples analysed at Draycote for UV260, turbidity, temperature, pH, chlorine demand, colour and total iron. Samples were prepared for analysis of THMs by DOC LABOR Germany. Analysis for UV254; colour; turbidity; manganese; aluminium; iron; TOC and chloride were also conducted by Severn Trent Laboratories.

Ozone

For the experiments involving ozone, the raw water feed to the MIEX plant was changed. The pressurised header supply flowed into a storage reservoir, from which a variable speed pump drew water into the MIEX plant. A small ozone generator was installed to add ozone to the header supply. Due to size constraints of the generator and infrastructure limitations, only 50% of the raw water entering the MIEX plant was treated with ozone. Jar test experiments were conducted with raw water that had been fully treated with ozone.

Jar Test Procedure

Samples of raw water and the ozonated water were collected for testing from the pilot plant operation. Testing was conducted on site at Draycote WTW using a six-paddle Stuart SW6 Flocculator. Two types of jar tests were conducted; Kinetic and Resin Loading Jar tests. The objectives of the jar tests were:

1) Contact Time / Kinetic Jar Test

- Determine if longer contact times would benefit UV abs./Colour/DOC removals
- Determine differences in kinetic performance of used resin versus virgin resin

2) Resin Loading Jar Test

- Determine appropriate resin service for Draycote water and any difference in that between the virgin and used resins;
- Establish the relationship between the batch jar test results and the continuous pilot plant results;

The jar tests were conducted with raw water; raw water pre-treated with 2ppm ozone and raw water pre-treated with 4ppm ozone. This was done to determine the effect of pre-ozonation on DOC/UV abs. /colour removal performance.

The procedures for the two types of jar tests were:

Contact Time / Kinetic Jar Test

- ➢ set 2 x 1 L jars with 10 mL settled virgin resin (i.e. 2 replica jars series for comparison);
- ➢ set 2 x 1 L jars with 10 mL used fresh resin;
- ➢ run jar tests for a total of 60 min mixing (i.e. contact time);
- ➢ samples are extracted from jars during mixing at the following times:
  - 0 min = raw water before the resin addition;
  - 2 min, 5 min, 10 min, 15 min, 20 min, 30 min, 60 min
- ➢ samples are extracted by a syringe (resin + water); the resin is then filtered out using a 45 um syringe filter; after filtering the sample, the syringe is flushed clean of resin – the resin from the syringe is discarded and not returned to the jars;
- ➢ filtered samples are subjected to colour and UV abs. analyses;

NB The capacity of the resin to adsorb organic material is explained by Bed Volumes (BV), whereby a set amount of resin (10ml in the jar test) is classified as one bed volume and the amount of water that the resin services is multiples thereof (in the jar test 1000 BV relates to 10 ml of resin treating 10 L of water).

Resin Loading Jar Test

- ➢ set 2 x 1 L jars with 10 mL settled virgin resin (i.e. 2 replica jars series for comparison);
- ➢ set 2 x 1 L jars with 10 mL used fresh resin;
- ➢ run all jar tests with 10 min mixing (i.e. contact time) followed by 5 min settling, before 950 mL supernatant is removed by decanting with care to minimise the resin loss;
- ➢ after the decanting, refill the jar with resin and with another 1000 mL of fresh raw water and repeat the mixing-settling-decanting procedure; repeat this at least 15 times; each jar tests corresponds to the resin service of 100 BV, hence 15 in a series corresponds to the service of 1500 BV;
- ➢ measure UV abs. and colour on each decanted water (i.e. both replica jar tests)

- the remaining decanted water is placed in a bucket and combined with other decanted waters;
- UV abs. and colour is measured and the following 100-250 mL samples taken from the combined waters: 500, 800, 1000, 1200, 1500 BV (i.e. after 5 jar tests, and then after 8, 10, 12 and 15); before these samples are measured/taken ensure the combined water is thoroughly mixed)

4.7 Dissolved Air Flotation

As part of the MIEX trial, a PUREC dissolved air flotation pilot unit (**Fig 4.8**) was incorporated to evaluate a downstream treatment process. The automated system had a flow rate equal to that of the MIEX plant output. Ferric sulphate was used as the primary coagulant, with hydrochloric acid used for pH correction.

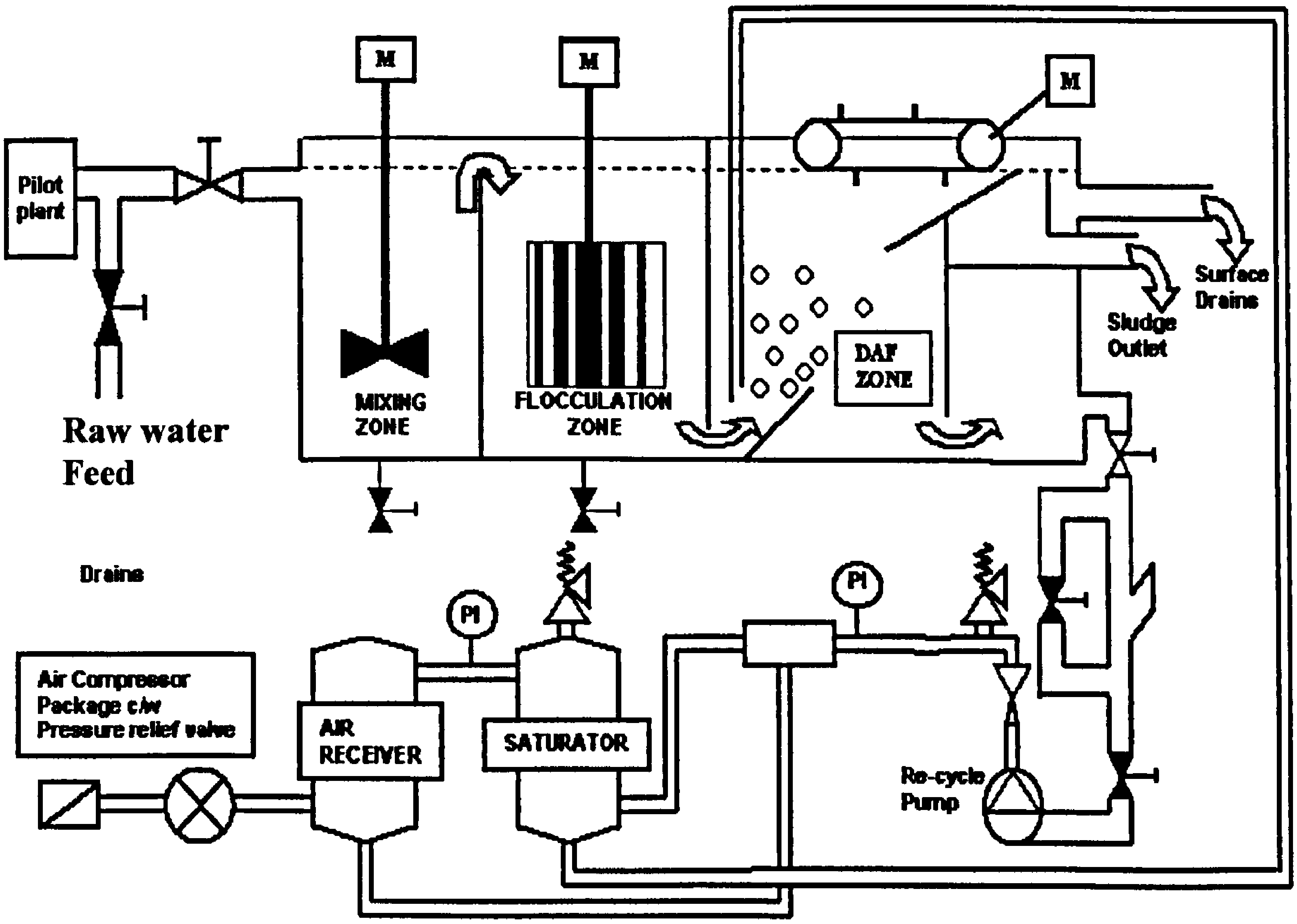


Fig 4.8. Schematic of the PURAC DAF pilot plant

The DAF unit was run in two modes; firstly with raw water, to evaluate the ability of DAF to treat the water; and secondly with MIEX treated water to evaluate the ability, if any, to further reduced the NOM content after MIEX. The DAF unit was run with varying levels of ferric sulphate, firstly without pH correction, and secondly with coagulation pH correction. This was done to evaluate a cost cutting regime whereby pH correction was eliminated.

As with the MIEX experiments, periodic samples were analysed for UV254, UV260, turbidity, temperature, pH, chlorine demand, colour, manganese, aluminium, iron, TOC and chloride. Samples were prepared for analysis of THMs by DOC LABOR Germany.

Chapter 5

Analysis of raw water

5.1 Introduction

Since all experiments conducted in this research use water sourced from reservoirs, it is imperative to understand the chemical and physical composition of the raw water. The main investigation involved water from Bamford WTW. This water has high levels of natural organic matter and low turbidity. The trend is in time varying but ever increasing TOC content; this is probably related to climate change and its effects on upland vegetation. Draycote WTW treats water with low turbidity and relatively low NOM (as calculated by UV254) but has high TOC. This water was also investigated.

It was important to characterise both types of water fully, before and after treatment, so that a better understanding of the treatment processes could be obtained.

5.2 Experimental

Materials and methods pertinent to this chapter were reported in **Chapter 4** of this thesis. In summary, the analysis of the Bamford water quality was conducted at the School of Chemical, Environmental and Mining Engineering, at the University of Nottingham, following procedures set out in **Chapter 4.2** (additional analysis was conducted by Severn Trent Water where stated). The analysis of Draycote water was conducted on-site at Draycote WTW using Severn Trent Water equipment.

5.3. Raw water analysis - Bamford Water

The results of the water analysis of samples taken over a two-year period are shown in **Table 5.1.** This water was collected from an inlet pipe from the reservoir at the treatment works.

Table 5.1. Analysis of Bamford raw water

	Minimum	**Maximum**
pH	5.93	6.37
TOC (mg/l C)*	5.6	9.94
Total Iron (μg/l)	333	420
Total Manganese (μg/l)*	37	108
Total Aluminium (μg/l)*	141	184
Iron – Filtered (μg/l)	222	283
Manganese – Filtered (μg/l)*	3.9	22
Aluminium – Filtered (μg/l)*	91	155
TOC – Filtered (DOC) (mg/l C)*	4.56	8.89
UV 254 (cm^{-1} abs.)	0.161	0.532
Turbidity (NTU)	0.19	8.9
Colour (mg/l Pt/Co)	34.8	94.2

- Analysis conducted by Severn Trent laboratories.

The pH measurements were slightly acidic; low values were expected, especially as the Derwent valley and Ladybower catchment areas consist of moorland, associated with runoff having high NOM levels.

The difference between TOC and filtered TOC (or DOC) indicates that although colloidal organic matter is present in the feed water, a significant proportion is dissolved

The variance in TOC levels is due to the time of year in which the samples were taken. The lower value was recorded during the summer months when there was reduced rainfall. The TOC is highest through the autumn and winter periods, as increased moorland runoff carries more NOM into the reservoir. Turbidity levels also highlight this seasonal variance. Although there is seasonal variation in TOC, there is not a vast difference. This could be explained by research conducted on Finnish lakes by Matilainen, A., N. Lindqvist, et al. (2002) who hypothesized that this was due to the size of the lakes having large residence times and were therefore not as susceptible to variations as river sources. The Derwent and Ladybower reservoirs are amongst the largest lakes in England.

Throughout the summer months, turbidity is low, but it increases significantly during the autumn/winter period. This can be explained by temperature inversion occurring in the reservoir during times of large changes in air temperature. Cold air temperature decreases the temperature of the surface water, changing the density of the water causing it to sink; as a consequence the warmer water at the bottom of the reservoir rises, disturbing the settled NOM and therefore increasing the turbidity in the WTW inlet water.

The levels of iron, aluminium and manganese were relatively stable over the period of the trial although increased during periods of high runoff. The main difference is between the total and filtered samples, indicating differences in the form of the species present. With iron, approximately 1/3 is colloidal in nature (probably organically bound) while 2/3 is dissolved iron species. Unfortunately, due to the analytical methods available, the exact form of the species was not able to be determined. The figures for aluminium again indicate a large proportion is dissolved.

However, manganese has a larger proportion of colloidal material, mainly organically bound (Severn Trent laboratory analysis). Manganese can create problems during the coagulation treatment process, as the manganese is displaced by the addition of ferric ions increasing the levels of manganese in the treated water. This problem is particularly pertinent at Bamford, as one of the reservoir feeder streams draws from an area of old mining activity; this is exacerbated by the feeder stream entering the reservoir near a treatment works inlet pipe.

The type of catchment area will also effect the molecular weight distribution of the NOM in the reservoir (Anderson et al (2000). DOC characterisation conducted by Severn Trent (**Table 5.2.**) showed the water contained mostly fulvic and humic acid fractions, which is expected, with upland reservoirs having a high percentage of humic and fulvic acids (Malcolm R. L. 1990). The hydrophilic neutral fraction of the water contributed 24%; this fraction has a significant impact on the treatment processes, as shown later in **Chapters 6 & 7.**

Table 5.2: DOC analysis of Bamford raw water (28/11/03)

DOC parameters	**mg/l**
Fulvic acids	3.8
Humic acids	1.3
Hydrophilic acids	1.2
Hydrophilic neutrals	2.1
Hydrophobic neutrals	0.4
Total	8.8

Analysis conducted by Severn Trent Water (method XAD fractionation)

The fact that Bamford water has a high percentage of charged organics makes it ideal for pre-coagulation and membrane filtration, as according to Sharp & Parsons, et al. (2005), the hydrophobic NOM fractions have a significantly higher charge density than the hydrophilic NOM fractions, whereas the hydrophilic non-adsorbed fraction has a negligible charge density, therefore the affinity of cationic hydrolysis products for the hydrophobic fraction is greater.

Although there is no figure given, Bamford WTW also has a problem with polysaccharides. Although the source of these is uncertain, they are abundant in the reservoir (seen as algal blooms on the surface of the water during the summer). This problem, taken in conjunction with the above analysis, shows that although in theory the treatment of Bamford water should be straightforward, there are many factors that have to be considered when treating this particular water.

5.4. Draycote Water

The results of the investigation into the water quality at Draycote WTW between July and October 2004 are shown in **Table 5.3.** The analysis is still ongoing at the time of writing this thesis.

The analysis shows that the reservoir has relatively low levels of iron, aluminium and manganese. The pH of the reservoir is fairly stable. The turbidity was low during the summer months but increased as the temperature of the water decreased; this is similar to Bamford water, with temperature inversion of the reservoir increasing turbidity and NOM content.

Analysis by UV254 and UV260 show organics that absorb at these particular wavelengths; UV254 measures the level of colour in the sample normally caused by high molecular weight humic substances. The amount of NOM as indicated by UV 254 and UV 260 is low during the summer, with the levels only increasing slightly during the colder period. For this investigation, the samples were passed through a 0.45μm filter before analysis, in effect removing large compounds. Online UV, which is not filtered and TOC analysis indicated higher levels of organics present in the water. The discrepancy could be due to other types of organics present. Further analysis was conducted.

Table 5.3. Analysis of Draycote water

Parameter	Minimum	Maximum
UV 254 (abs)	0.006	0.322
UV 260 (abs)	0.008	0.221
Online UV %	12.32	14.38
Online UV (mg/l C)	8.32	9.77
Colour (Hazen)	2.9	15.5
Turbidity (NTU)	0.56	11.6
pH	8.48	8.86
Temperature (degrees °C)	10.5	20.9
TOC (as C mg/l)*	3.86	7.83
Total Aluminium (µg/l)*	<5	20
Total Iron (µg/l)*	<7	120
Total Manganese (µg/l)*	5	28
Chloride (µg/l)*	49.8	50

- Analysis conducted by Severn Trent Laboratories.

To investigate the types of organics present, Gas Chromatography-Mass Spectrometry analysis was conducted at the University of Nottingham. A sample of water (1 L) was divided into five aliquots (200 cm^3), and each was extracted into an equal volume of dichloromethane (DCM; 5x 200 cm^3 extracts). The extracts were combined and the solvent evaporated at ambient temperature. **Fig 5.2** shows the Total Ion Chromatogram of the Draycote water.

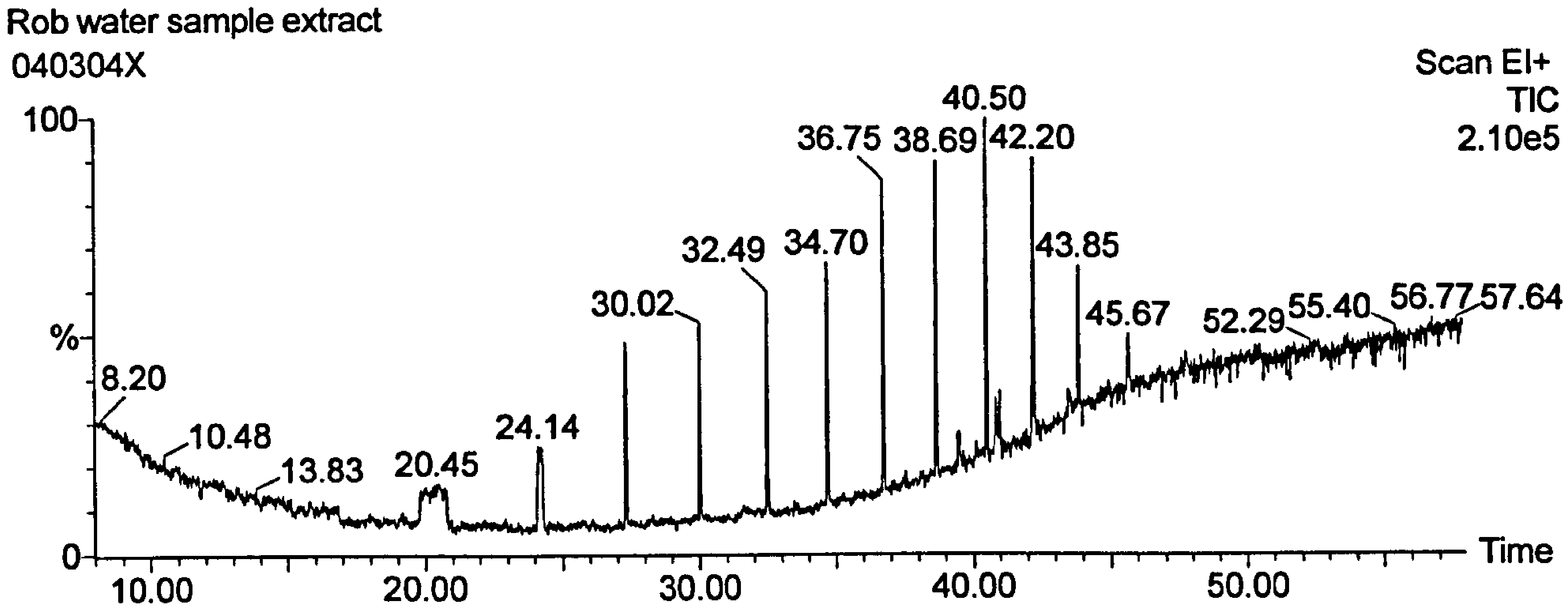


Fig 5.2. Total Ion Chromatogram of the Draycote water.

To investigate the various peaks, a GC/MS was conducted with ion mass 73 (m/z). An m/z of 73 is indicative of silicate (**Fig 5.3**).

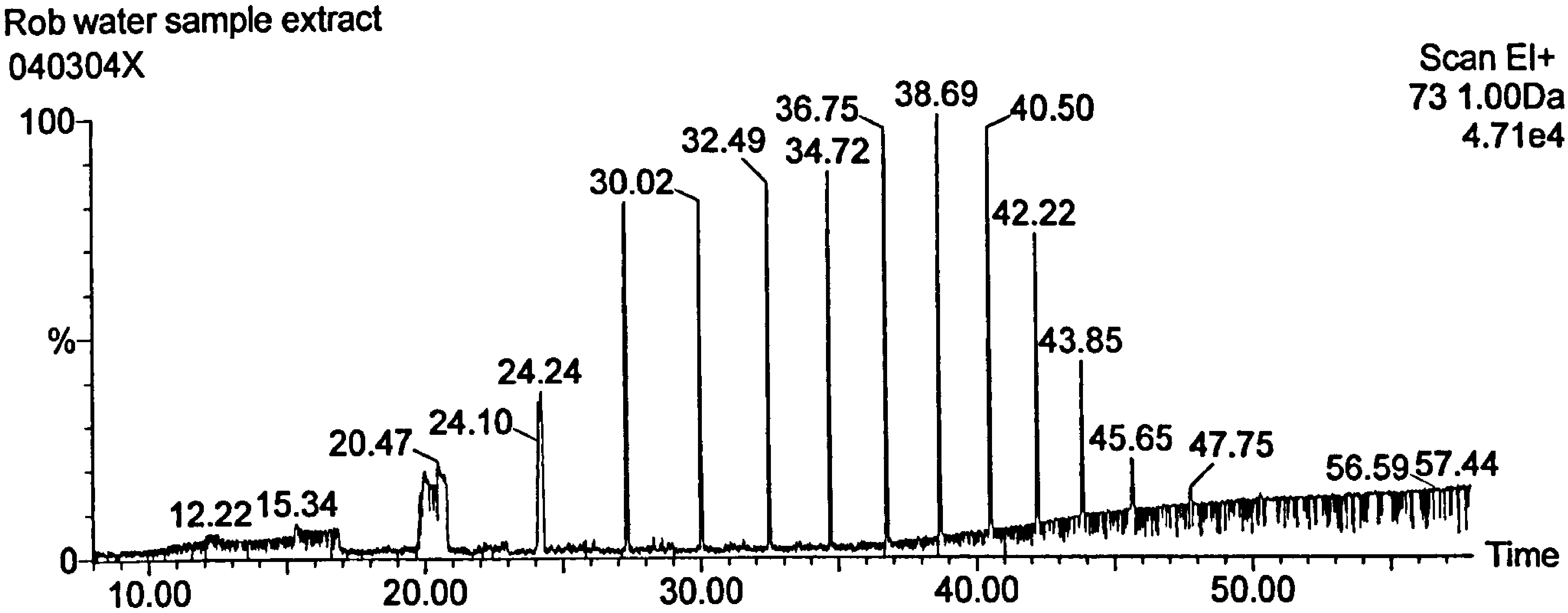


Fig 5.3. Mass Chromatogram of m/z 73, indicative of silicates

The similarities between the results of **Fig 5.2** and **5.3** indicate that silicates are the largest component of particulates in this water. This would be expected in surface water, where particulates of soil are normally present. However, this does not explain why there is a discrepancy in organic levels between filtered UV254 and TOC analysis. **Fig 5.4** shows a mass chromatogram of m/z 149. This particular ion mass is indicative of phthalates

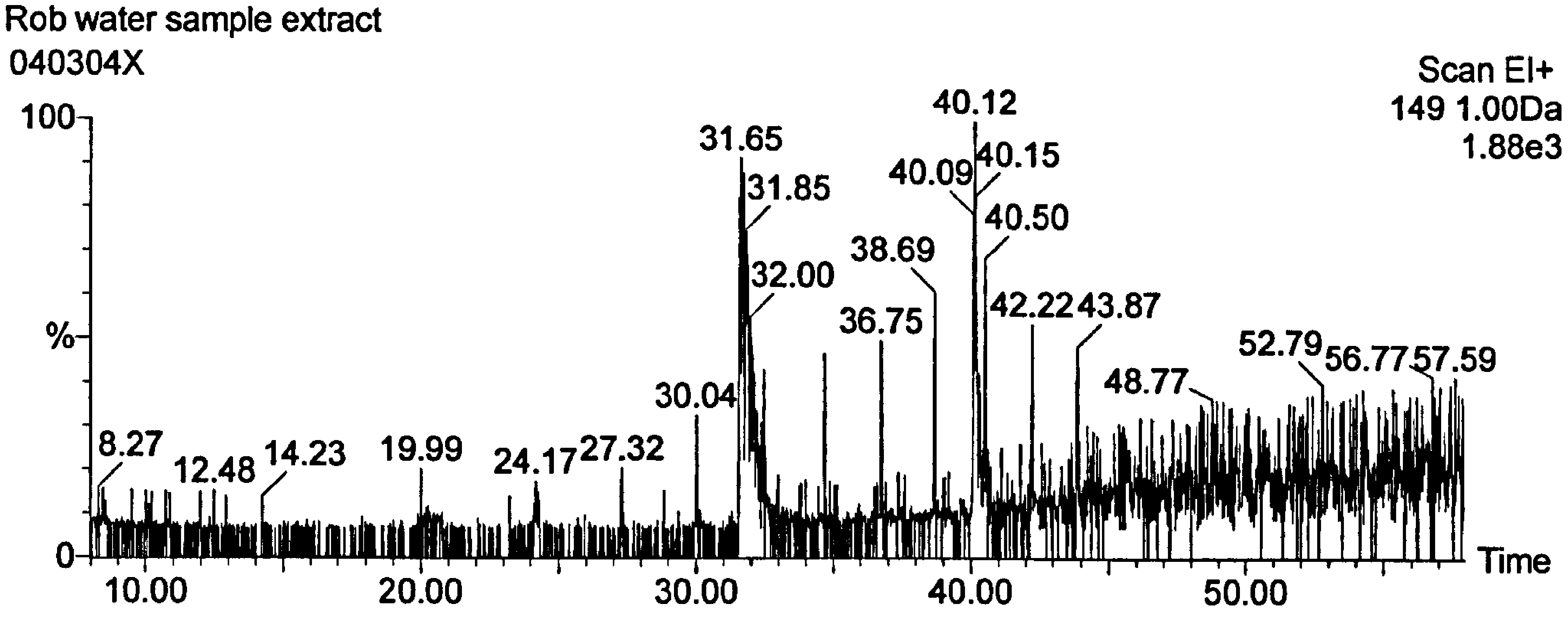


Fig 5.4 Mass chromatogram of m/z 149, indicative of phthalate

The results obtained from a GC/MS of m/z 149 indicate that phthalates are present in the water sample. We were not able to determine the exact nature of the phthalates present due to time constraints and the need for phthalate standards, although the most common environmental contaminants are di-2-ethylhexyl phthalate, di-*i*octyl phthalate, and di-*i*-decyl phthalate (Staples C. A. et al., 2000). Further analysis of the type of phthalate present is required.

To investigate the organic nature of Draycote water further, TOC-Characterization was conducted by DOC-LABOR, Germany on behalf of Severn Trent. **Table 5.4** shows the organic composition of the raw water. As with low turbidity waters, the main organic constituent is DOC, of which over 90% is hydrophilic in nature.

The hydrophilic fraction is composed of Polysaccharides (including amino sugars, polypeptides and proteins); Humics (molecular weight ~1000 g/mol.); Building Blocks (humic hydrolysates with molecular weight between 300 – 450 g/mol.); Neutral Amphiphilics (alcohols, aldehydes, ketones and amino acids) and low molecular weight organic acids.

Table 5.4 Characterization of Draycote water TOC.

TOC					
	TOC	**DOC**	**POC**		
Ppb	6428	6096	332		
% TOC	100	94.8	5.2		
DOC	**Hydrophobic**	**Hydrophilic**			
Ppb	158	5938			
% DOC	2.5	92.4			
Hydrophilic Fraction	**Polysaccharidic**	**Humics**	**Building Blocks**	**Neutral Amphiphilics**	**LMW acids**
Ppb	750	2744	1311	1089	45
% Hydrophilic	11.7	42.7	20.4	16.9	0.7

Method: Liquid Chromatography – Organic Carbon detection (LC-OCD), Calibration on basis of "Suwannee River" Standard IHSS-FA und IHSS-HA.

Unlike Bamford water, which has a large proportion of humic and fulvic acids (~70%), Draycote contains only ~40%; these large molecular weight organics are relatively easy to remove using conventional treatment methods. However Draycote contains a high proportion of building blocks and neutral amphiphilics, as well as polysaccharides. This makes the treatment of Draycote water difficult, as according to Kimura, K., et al. (2004), polysaccharides/protein like fractions of organic substances cannot be efficiently removed by coagulation; and in terms of membrane filtration, Makdissy et al. (2004) stated that the fouling contribution by humic-like materials was dependant on their origin and nature. Polysaccharides, proteins and amino sugars largely present in humic-like structures, play an important role in UF membrane fouling.

This was expanded on by Pikkarainen et al (2004) in their research, they stated neither clarification nor PC-MF were effective in removing low molecular weight UV254-absorbing organic materials. Their pilot scale tests indicated that coagulated raw water contained hydrophilic acid and hydrophilic non-acid fractions, which were partly adsorbed onto the membrane.

An alternative means of treating Draycote water may be with magnetic ion exchange. Humbert et al. (2005) showed that MIEX® was able to eliminate both high and part of low MW UV absorbing NOM, while only high MW organic molecules were preferentially removed by coagulation/ flocculation.

Both Bamford and Draycote water combines low turbidity with high organic content. However, the differences in the nature of the organic content provide different challenges in determining the best possible treatment processes. This thesis investigates the use of pre-coagulation and ultrafiltration, as well as magnetic ion exchange at looking at the best treatment option available.

Chapter 6

Optimisation of the Coagulation Process

6.1 Introduction

There have been many research articles published on the subject of coagulation, and as shown in **Chapter 2.10** the role of coagulation combined with membrane filtration has seen increased interest. Although all the articles mention optimizing the coagulation regime in terms of pH, coagulant dose and mixing regime, in relation to NOM removal. The question remains as to the effect on membrane filtration if the coagulation is not optimal, specifically the role of excess coagulant dose on membrane filtration, particularly during periods of cold temperature.

To evaluate the impact of excess coagulant on membrane filtration, it is important to first optimize the coagulation performance. In this chapter, optimisation refers to the conditions that provide the best performance for the removal of natural organic matter, in terms of UV254 abs. (as representing TOC) removal, rather than economic considerations.

Optimising the coagulation process normally involves standard jar-test procedures with varying levels of coagulant while maintaining the optimum pH value, and using TOC removal as the benchmark after the flocs have settled out of solution.

As has been already mentioned, conventional jar testing for clarification is a very well explored phenomenon and is widely published. With this in mind, this chapter will only include a summary of the investigation into optimising dose, pH and mixing regime. A more detailed account of the investigation into optimising the dose; pH and mixing regime can be found in **Appendix A.**

As the focus of this research is the removal of flocs by ultrafiltration, rather than by normal clarifier procedures (i.e. floc settling), the optimisation of coagulation has to be a compromise between TOC removal, operating times and floc size. As it was not important to form macro-flocs, but rather micro-flocs, the optimisation of coagulation described in this chapter represents the conditions that provide the greatest removal of NOM in the shortest possible time, while allowing the flocs to grow large enough to remove the coagulant and any residual iron.

This chapter will first summaries the basic results of the optimum dose; pH and mixing regime from the standard jar tests and then focus on the removal of NOM and incomplete coagulation in relation to downstream membrane filtration.

6.2 Summary of experimental protocols

Materials and methods pertinent to this chapter were reported in **Chapter 4.4** of this thesis. Coagulation experiments were conducted with ferric chloride, ferric sulphate and alum on raw water from Bamford WTW and Draycote WTW. The research involved optimisation of pH, coagulant dose, mixing regime and the effect of temperature on coagulation performance.

6.3 Results

6.3.1 Optimum conditions of pH, dose and mixing regime

Standard jar-test experiments, as well as photometric dispersion analysis, were conducted with ferric sulphate, ferric chloride and alum on Bamford water. Coagulation of Draycote water was conducted with ferric sulphate. **Table 6.1** shows the optimum pH value, coagulant dose and the mixing regime for each coagulant. The mixing regime is given in seconds as the time taken for the PDA to reach maximum ratio value, as discussed in **Chapters 2.10.4** and **4.3**.

The complete set of jar test results and analysis is shown in **Appendix A.**

Table 6.1 Optimum coagulation regimes as determined by standard jar test methods

Water Source	Coagulant	pH	Coagulant dose	Rapid mix (250rpm) Seconds	Slow Mix (30rpm) Seconds	Permeate quality UV254 cm^{-1}
Bamford	Ferric sulphate	4.8	2.5 mg/l Fe^{3+}	30	200	0.036
	Ferric chloride	5.0	2.5 mg/l Fe^{3+}	30	300	0.037
	Alum	6.7	6.5 mg/l Al^{3+}	30	400	0.043
Draycote	Ferric sulphate	5.5	2.4 mg/l Fe^{3+}	30	350	0.105

The results for optimising the pH are in accordance of published literature. Adin A. et al., (1998) showed that for ferric ions, the predominant coagulation of adsorption and charge neutralisation occurs between pH 3 – 5. Alum on the other hand performs best at pH 6 – 7, the predominant coagulation mechanism being sweep or adsorption of micro-flocs.

The amount of coagulant required is dependent on the type of water to be treated. With Bamford water, the ferric coagulants outperform alum. With this type of raw water, alum performs poorly, with more than double the mass of coagulant needed to reach the performance of the ferric salts. As the optimum regime is based on performance, the best coagulant for treating Bamford water is ferric sulphate.

As the optimum coagulant dose is generally associated with a near zero zeta potential, the results for Bamford water show that the optimum ferric sulphate dose, lies between 2.2 and 2.8 mg/l Fe^{3+}, the value being dependant on the water quality.

With regard to the mixing regime, the results show that for all coagulants 30 seconds is an adequate time to disperse the coagulant and produce the maximum number of flocs possible. The main difference is in the time taken during slow mixing for the flocs to reach their highest ratio value. Ferric sulphate reached maximum performance quicker than the other coagulants.

The difference in treated water quality, with ferric coagulants outperforming alum, is again shown in literature. Volk C et al., (2000) showed that at lower pH, ferric coagulants performed generally better for the removal of organic carbon than alum.
Pikkarainen A. T. et al., (2004) revealed that ferric salts were more effective than aluminium salts in precipitating the IMW aromatic NOM fraction; and the least effective coagulant in removing this fraction was alum.

The water quality from coagulation of Draycote water is significantly lower; this is due to the large percentage of organic neutrals and polysaccharides present in the water, which cannot be removed by hydrolysis products.

6.3.2 Removal of NOM

In reviewing the publications into coagulation and membrane filtration, the main difference between the articles is in the coagulation methodology, specifically the approach to the mixing regime (**Chapter 2.10**). However, Judd and Hillis (2001) indicated that flocs only need to grow to a certain critical floc size prior to challenging a microfiltration membrane. They stated that this is due to the sub micron pore size of the membrane, therefore only requiring the flocs to growth to around 2μm and can be reached with only 30 seconds of rapid mixing, as relating to NOM removal.

Since this current work is interested in removing NOM by ultrafiltration membranes, the role of rapid mixing in the removal of NOM was investigated. **Fig 6.1** shows the removal of NOM during the rapid mixing phase. In this experiment with 3 mg/l Fe^{3+}, the rapid mixing period was extended to 480. Samples were collected periodically throughout the experiment and then filtered through Whatman 2 filter paper (pore size 8 μm) to remove the flocs; the sample was then analysed by UV254 for residual NOM levels.
The mixing was started after 20 seconds, so that a PDA base line could be established.

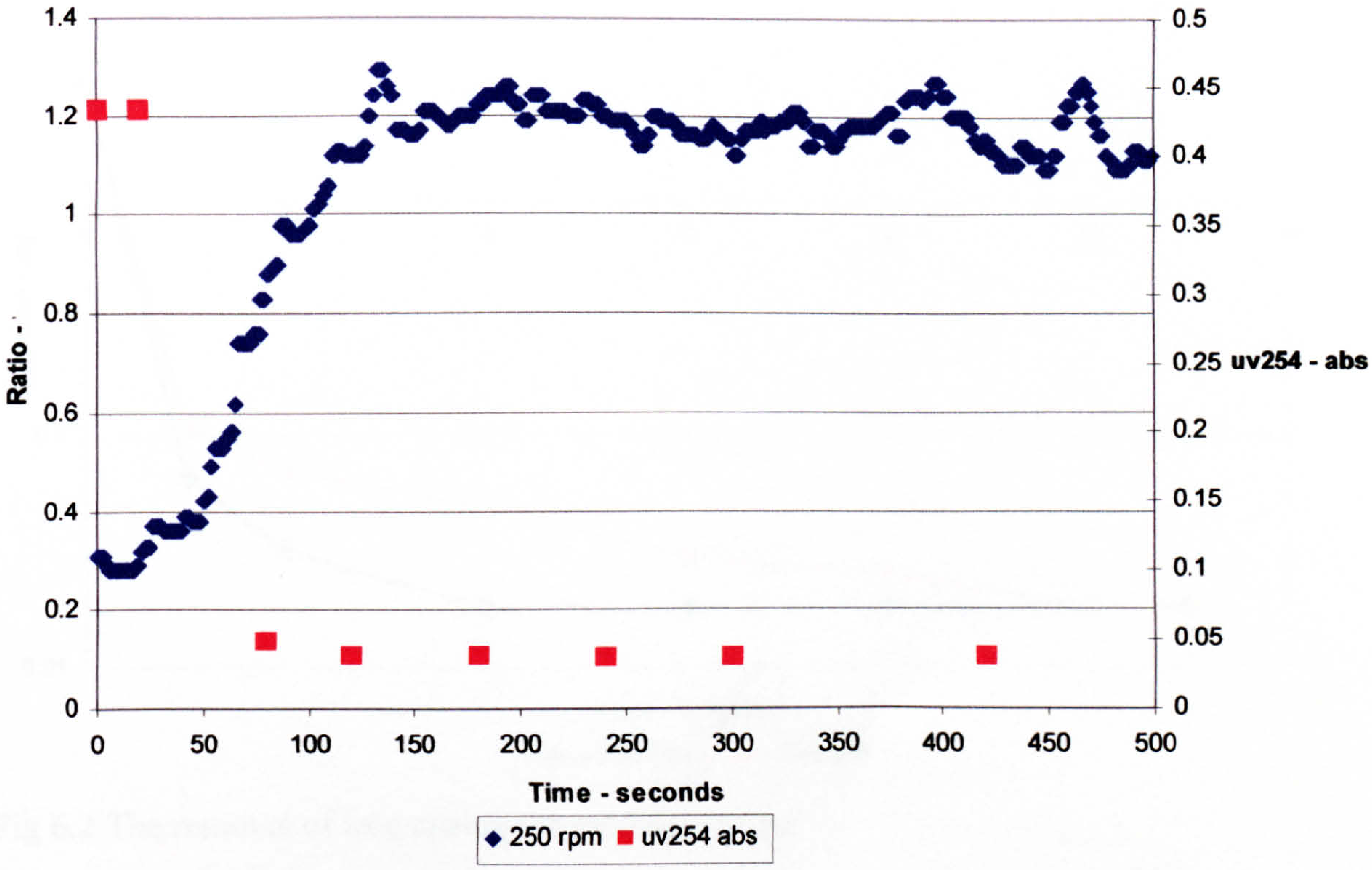


Fig 6.1 NOM removal by rapid mixing

The results show that the formation of flocs reduces the levels of NOM to a steady level after only 60 seconds of rapid mixing. However, the level of NOM does not reach zero, due to organic species present, which cannot be removed by coagulation. Although there is no regulatory limit on TOC (UV254) at present, the treated water does comply with acceptable regulatory levels in terms of colour.

However, as the raw water contains species other than NOM, in particular colloidal and dissolved iron, and ferric sulphate is used as the coagulant, it was important to study the removal of iron during the mixing process. This is important, as colloidal iron has been shown to affect and clog the membrane (Soffer Y et al 2004). Experiments were conducted on the removal of iron by rapid mixing followed by a period of slow mixing; varying rapid mixing rates were used (**Fig 6.2**). In these experiments 60 seconds of rapid mixing was followed by a period of slow mixing at 30 rpm.

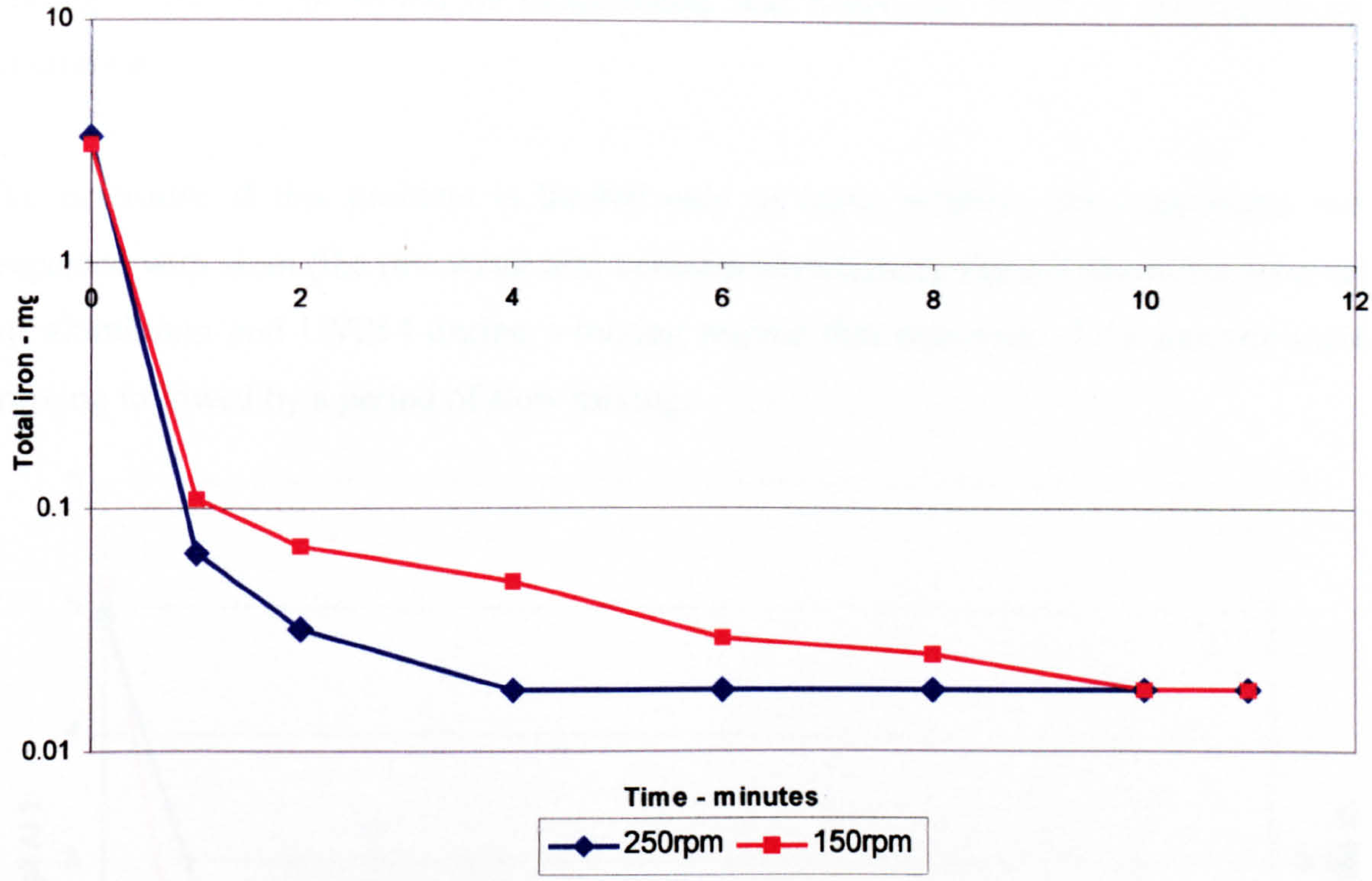


Fig 6.2 The removal of iron during the mixing process

The raw water sample in this experiment contained 0.333 mg/l total dissolved iron and 3 mg/l Fe^{3+} of ferric sulphate was used as the coagulant. The results show that, at the higher shear rate, all the coagulant is dispersed and formed into flocs that are larger than 8 microns after the period of rapid mixing; however, there still remains dissolved iron present in the sample.

The rate of rapid mixing affects the rate of floc growth during slow mixing. This is highlighted in **Fig 6.2** by the time taken to remove the excess iron by the different rapid mixing rates. The faster the rapid mix the greater the growth of flocs during slow mixing, and as a consequence, the quicker the removal of dissolved iron. However a period of slow mixing is required to increase the size of flocs and remove the remaining iron by enmeshment in the growing flocs. At the higher shear rate the time required to remove the iron is 3 minutes.

It should be noted that as there is a maximum number of flocs formed by precipitation of iron hydroxide flocs at any given shear rate, overdosing with coagulant will leave excess iron in solution, and as a consequence the problem of removing excess iron through enmeshment would be exacerbated, and hence the effect on the membrane increased.

To determine if this problem is limited only to ferric sulphate, the experiment was repeated with alum (the raw water also contains aluminium). **Fig 6.3** shows the removal of aluminium and UV254 during a mixing regime that consisted of 60 seconds rapid mixing followed by a period of slow mixing.

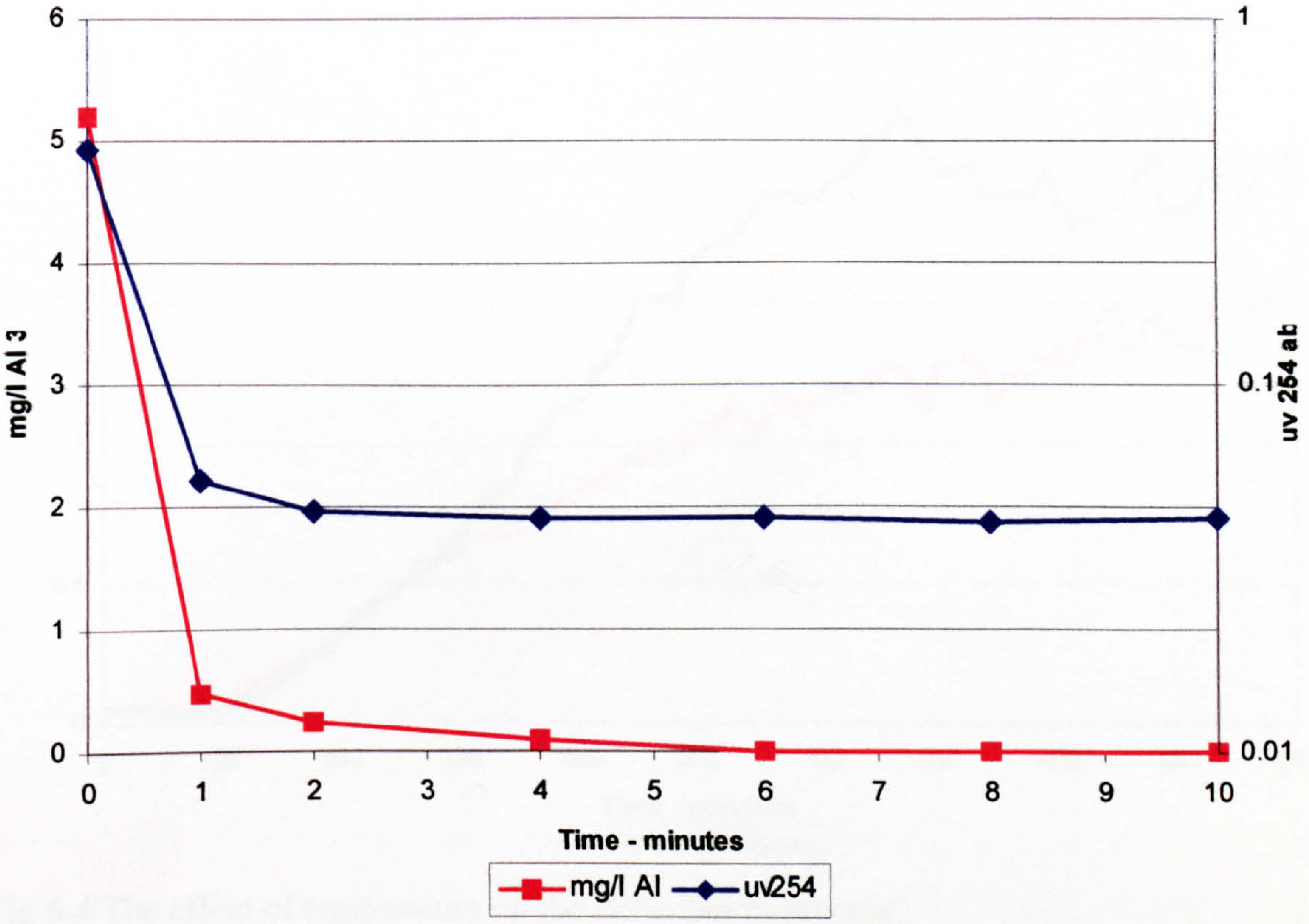


Fig 6.3 Removal of aluminium and UV254 abs. during the mixing process

The removal of excess aluminium, similar to iron, requires a period of slow mixing to enmesh the excess in the growing flocs. The amount of aluminium after rapid mixing was 0.479 mg/l; as the aluminium in the raw water was only 0.118 mg/l, this indicated that for this experiment excess coagulant was used. This highlights the need for control not only over the mixing regime but also the amount of coagulant used - no matter what the type of coagulant used.

These experiments were conducted during the summer period, when the temperature of the water was high. It was imperative to look at how temperature affects the growth of flocs and hence the removal of excess coagulant.

6.3.3 The temperature effect

The seasonal variations in temperature have a direct effect on the orthokinetic flocculation. As the temperature decreases, so to does the flocculation performance. An experiment was conducted using 3mg/l Fe^{3+} (ferric sulphate) at a pH of 4.8. One minute of rapid mixing was followed by a period of slow mixing (**Fig 6.4**). The lower temperature experiment was controlled throughout by application of ice packs.

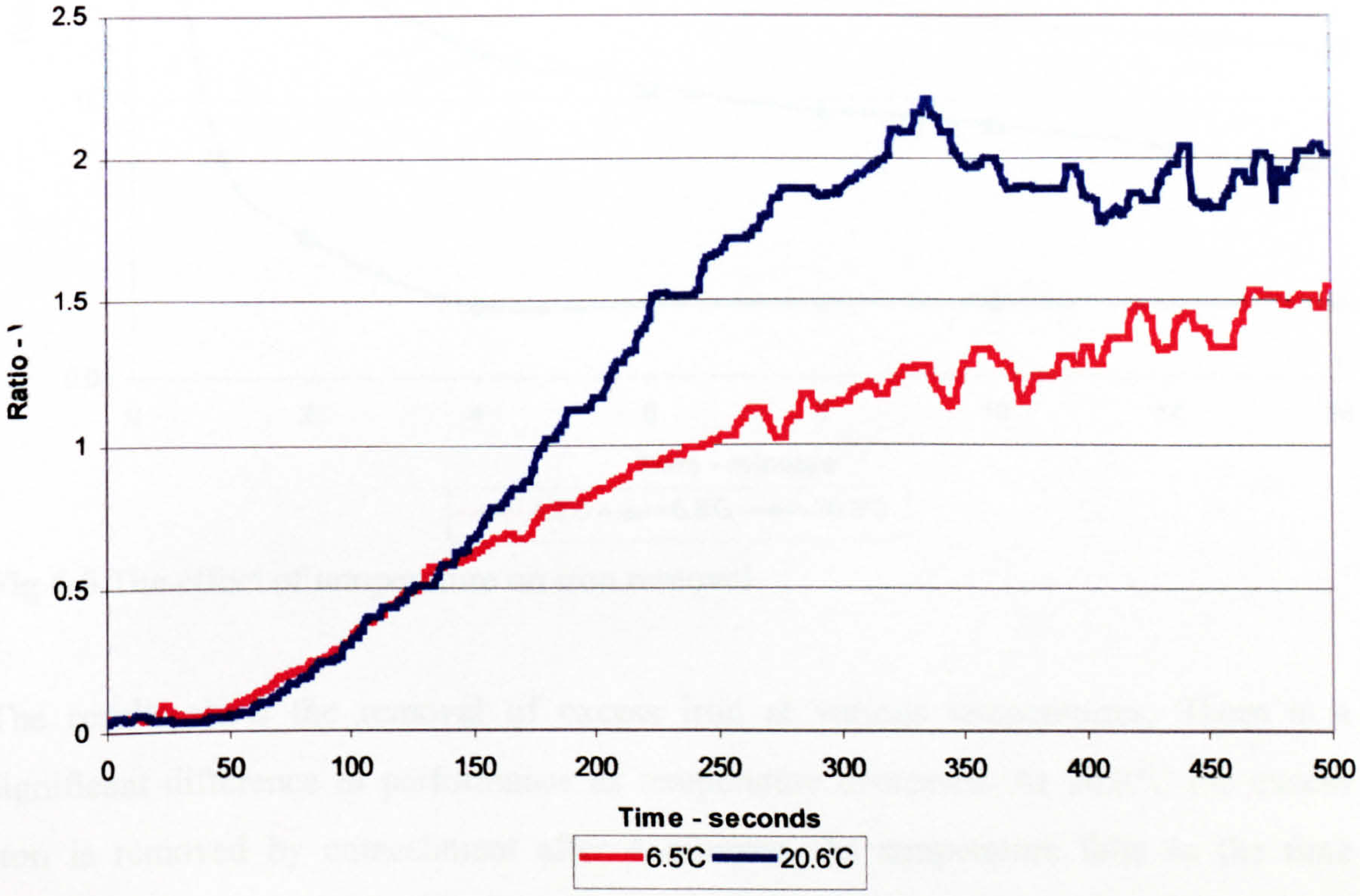


Fig 6.4 The effect of temperature on the flocculation process

The results show that the initial coagulation process is not greatly affected by temperature; however, temperature does affect the rate of flocculation. The lower temperature causes the formation of smaller and denser flocs. The reduced size of the flocs diminishes the performance of 'sweep flocculation', as there is a reduced surface area to enmesh the particles. This will have a significant impact on the removal of the excess iron fraction (**Fig 6.5**). The experiments on temperature effects involved samples of raw water being cooled to various temperatures before the experiment started. In these experiments 60 seconds of rapid mixing was followed by a period of slow mixing at 30 rpm.

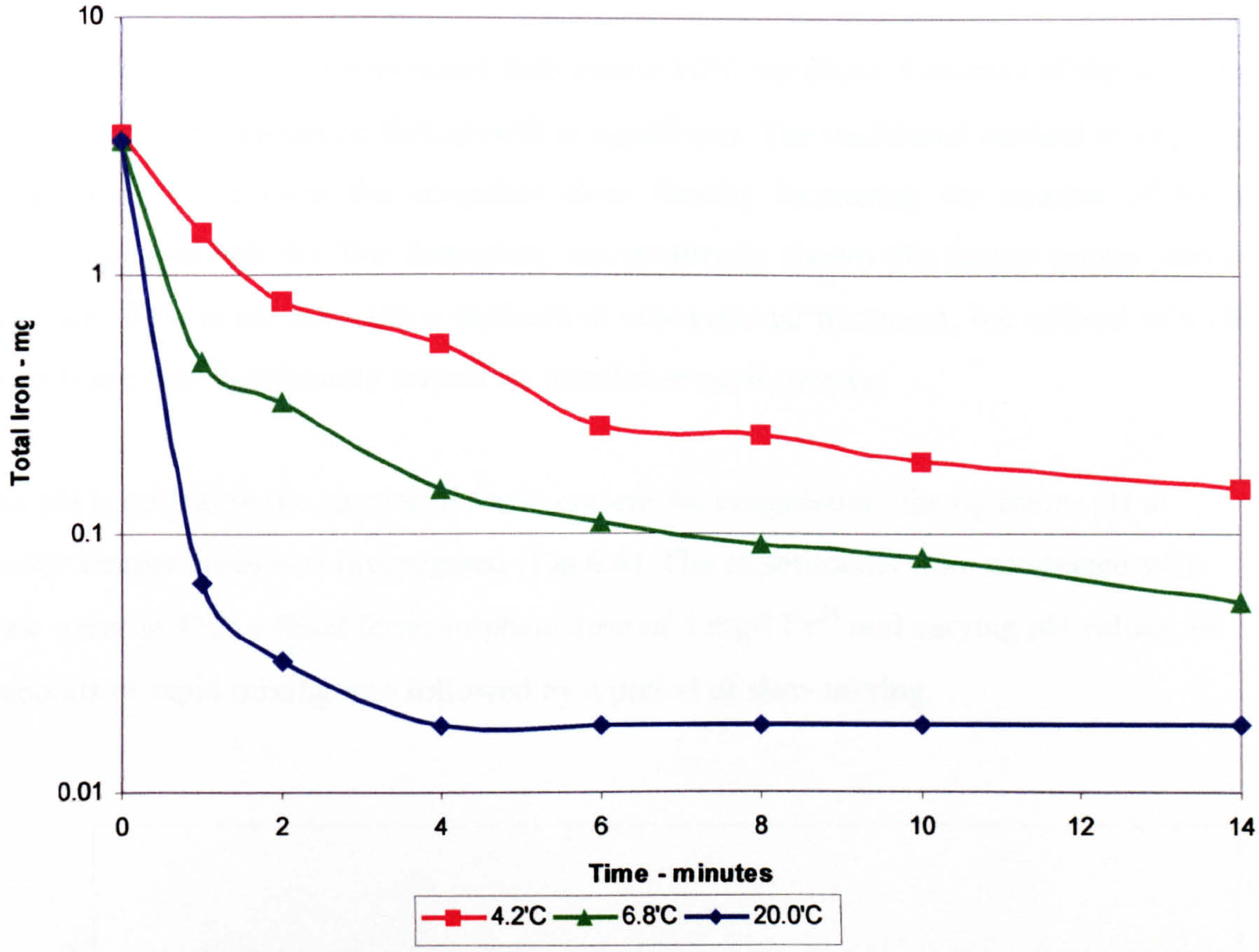


Fig 6.5 The effect of temperature on iron removal

The results show the removal of excess iron at various temperatures. There is a significant difference in performance as temperature decreases. At 20.0°C the excess iron is removed by enmeshment after 4 minutes. As temperature falls so the time required to remove the iron increases. At 4.2°C ferric sulphate remains un-flocculated even after 14 minutes; a longer period of rapid mixing at lower temperatures may be a solution.

These results were indicative of the performance at the Bamford Zenon pilot plant. A water sample (5°C) was taken from the membrane tank, the flocs were filtered out using Whatman 8 micron filters and the water was tested for iron. The results showed 0.3 mg/l iron was present in the water that enters the membrane. This leads to the conclusion that the fouling problems encountered at the pilot plant during the winter period are caused by the incomplete removal of iron during the mixing process.

The question remains of how to improve the performance of coagulation at low temperatures, so the effect on membranes is lessened.

In the UK as the water temperature falls below 10°C for about 5 months of the year, the problem of temperature on floc growth is significant. The traditional method to improve coagulation is to raise the coagulant dose thereby increasing the amount of ferric hydroxide available for floc formation, but as already shown this leaves excess iron in solution. This is not normally a problem in conventional treatment, but upfront of a UF membrane can significantly impact on membrane performance.

As pH is critical in the species of ferric present for coagulation, the optimum pH at lower temperatures was investigated **(Fig 6.6)**. The experiments were conducted with raw water at 4°C; a fixed ferric sulphate dose of 3 mg/l Fe^{3+} and varying pH values. 60 seconds of rapid mixing was followed by a period of slow mixing.

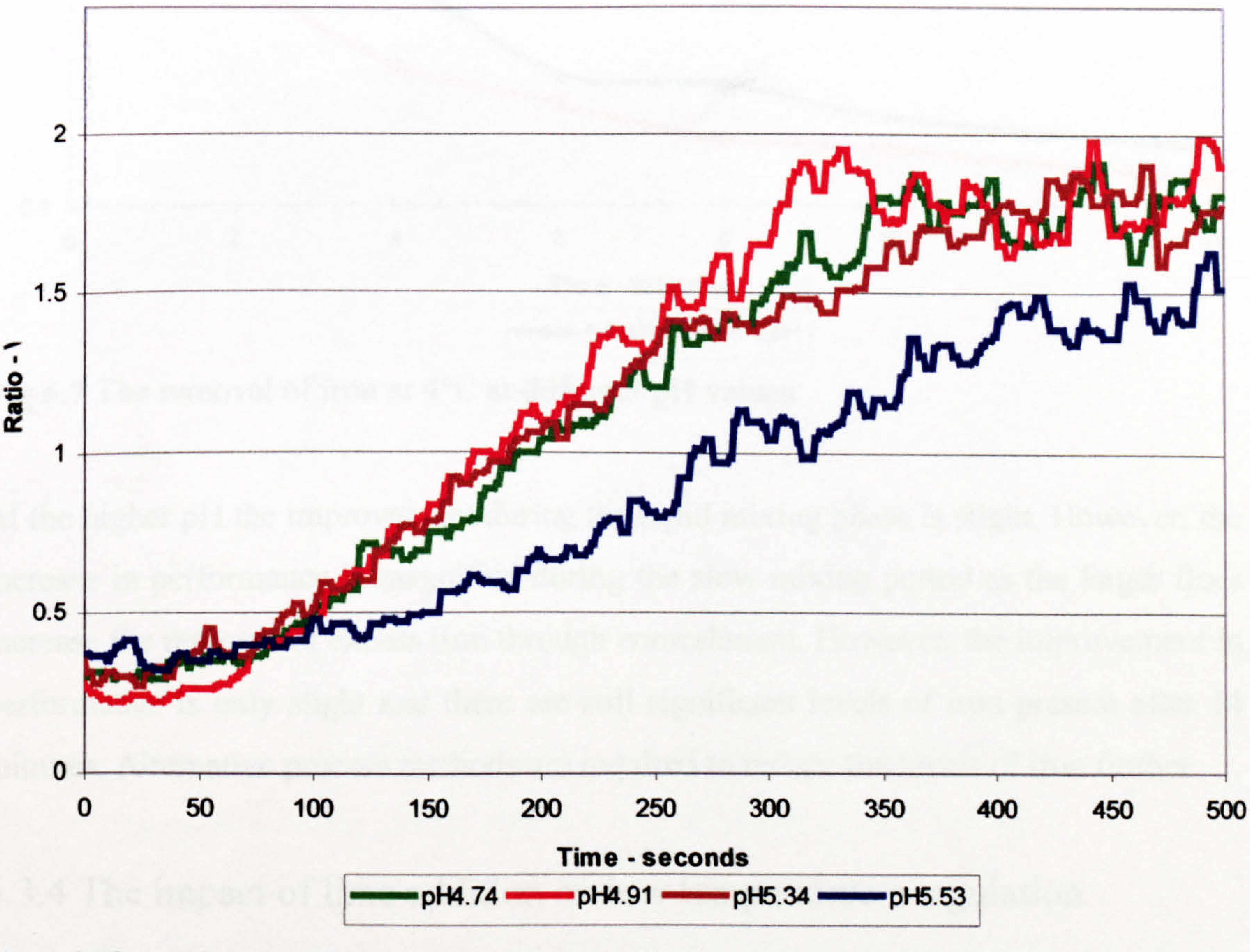


Fig 6.6 The optimum pH at low water temperatures

The results show that the optimum pH of coagulation with ferric sulphate shifts towards alkalinity by 0.1 pH units i.e. 4.9 compared with a pH at 20°C of 4.8. This increase in pH has been shown by many researchers (see **Chapter 2.8.3**) and may be due to the effect on the precipitation and solubility of ferric sulphate at the lower temperature (Kang L. S. and Cleasby J. L., 1995). **Fig 6.7** shows how this higher pH effects the removal of iron. The experiments were conducted with raw water at 4°C; a fixed ferric sulphate dose of 3 mg/l Fe^{3+} and varying pH values. 60 seconds of rapid mixing was followed by a period of slow mixing.

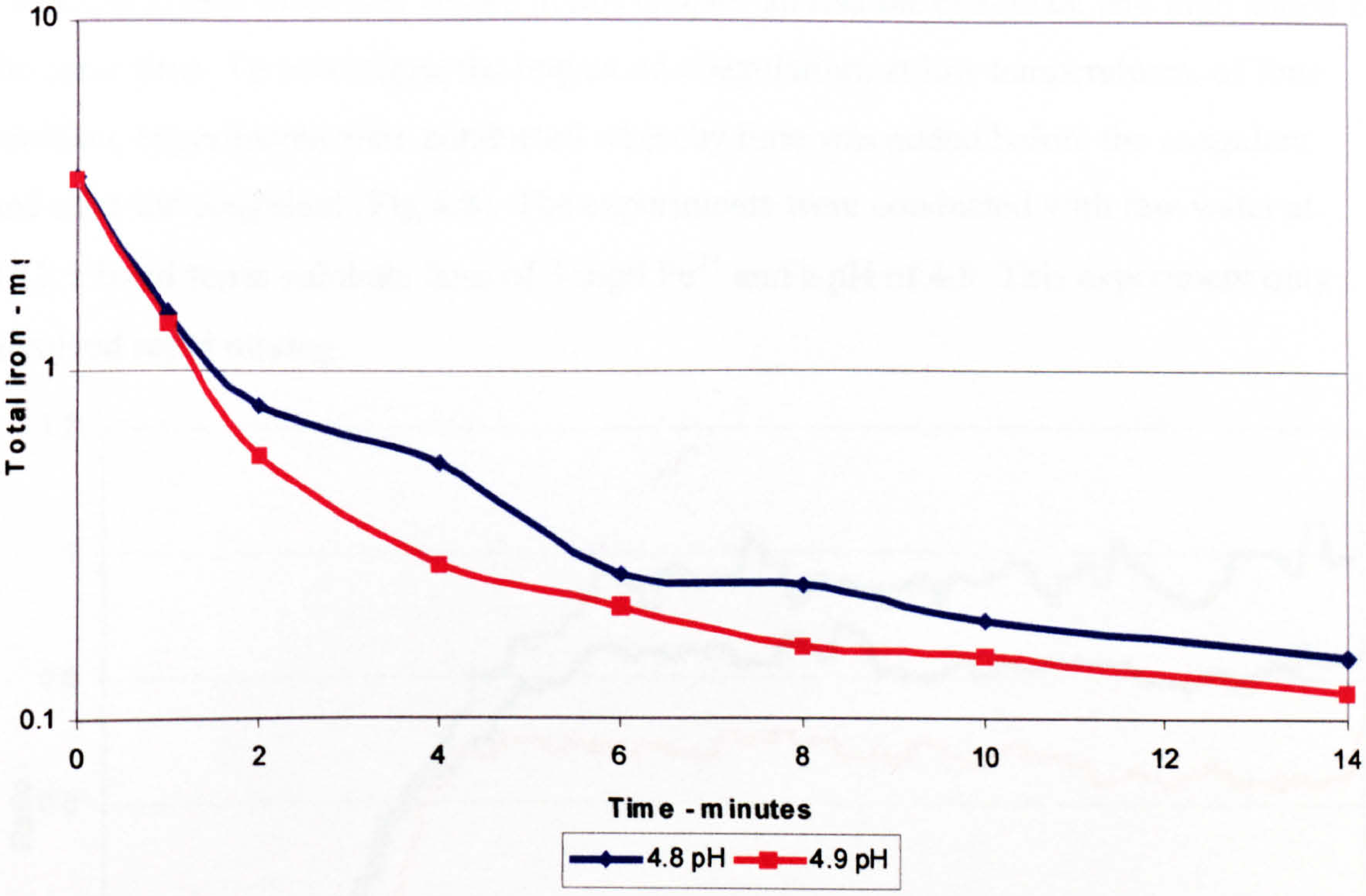


Fig 6.7 The removal of iron at 4°C at different pH values

At the higher pH the improvement during the rapid mixing phase is slight. However, the increase in performance is magnified during the slow mixing period as the larger flocs increase the removal of excess iron through enmeshment. However, the improvement in performance is only slight and there are still significant levels of iron present after 14 minutes. Alternative process methods are required to reduce the levels of iron further.

6.3.4 The impact of lime addition on low temperature coagulation

One of the problems with this type of water is its' low turbidity levels. Particulates in water aid coagulation as they provide nucleating sites on which flocs can form and grow. Low turbidity waters lack these seeding points and although at high temperatures this is not a problem; at low temperatures this lack of particulates can hinder the coagulation process. The addition of lime for pH correction can remedy this problem due to its colloidal nature. There has been numerous studies on the impact lime has on coagulation, as well as debate on where in the process stream the addition of lime has the greatest impact. However, the impact of lime on coagulation at low temperatures has not been fully investigated.

The experiments discussed before in this chapter all had the coagulant and lime added at the same time. To investigate the impact on coagulation, at low temperatures, of lime addition, experiments were conducted whereby lime was added before the coagulant and after the coagulant (**Fig 6.8**). The experiments were conducted with raw water at 4°C; a fixed ferric sulphate dose of 3 mg/l Fe^{3+} and a pH of 4.9. This experiment only involved rapid mixing.

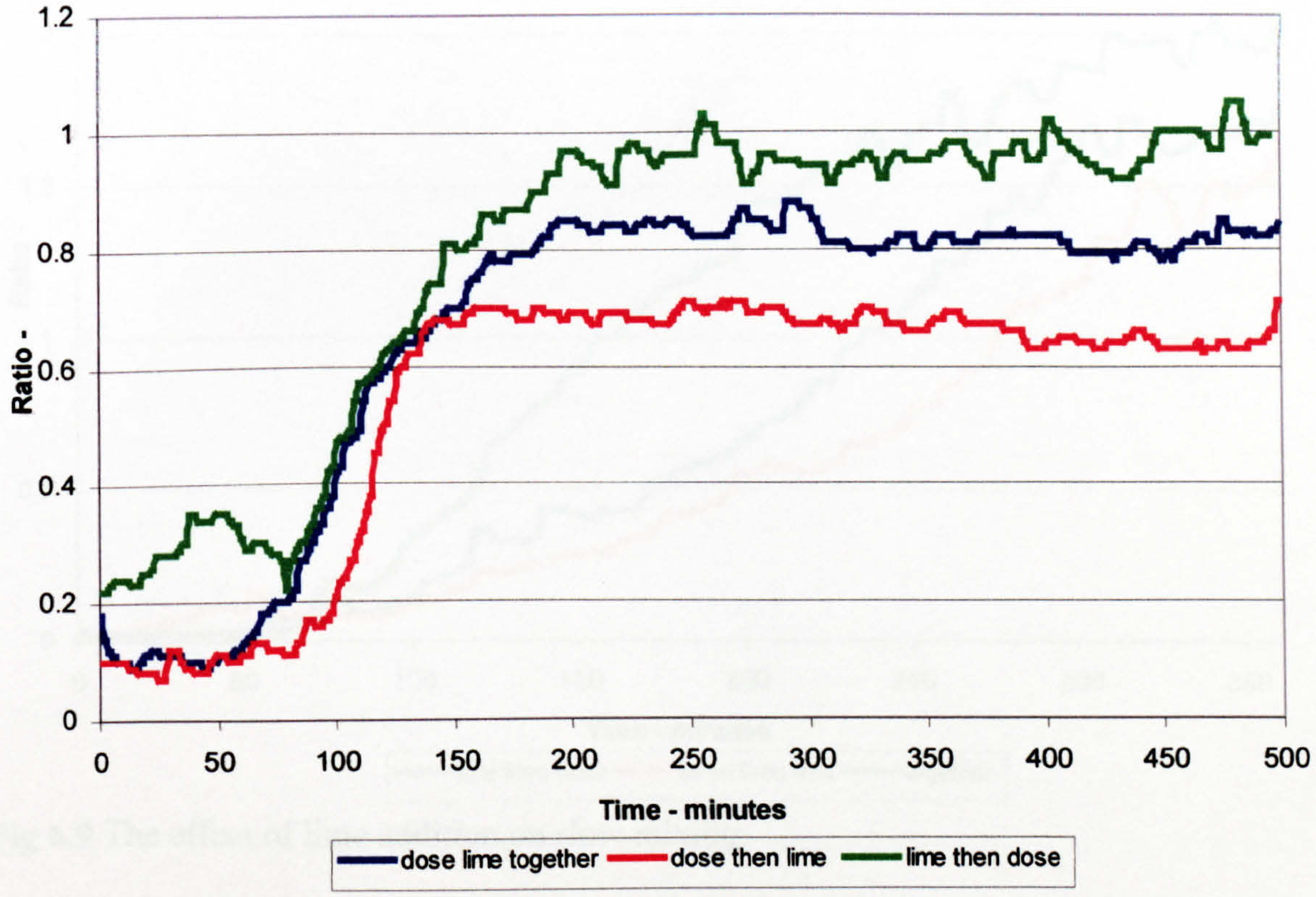


Fig 6.8 Impact on position of lime addition on floc formation and growth

The results show that the point of lime addition, in the coagulation process, is important. When lime is added first, the colloidal nature of the lime increases the initial ratio value before the addition of coagulant. This combination achieves the greater rate of floc growth when compared to when the coagulant and lime are added together. The use of coagulant before the addition of lime achieves the slowest floc growth rate. The results indicate that the colloidal nature of the lime provides nucleating site on which the flocs can more readily form and grow.

The most significant difference is in the maximum ratio values reached. As stated before, the ratio value is an indication of floc size; and as all three experiments were conducted at the same mixing speed; it is indicative of floc strength and integrity. When lime is added before the coagulant, the flocs formed are stronger and less susceptible to floc break-up due to the forces of shear. **Fig 6.9** shows the impact this stronger and larger floc has on flocculation. In this experiment, 60 seconds of rapid mixing at 250 rpm was followed by a period of 30rpm slow mixing.

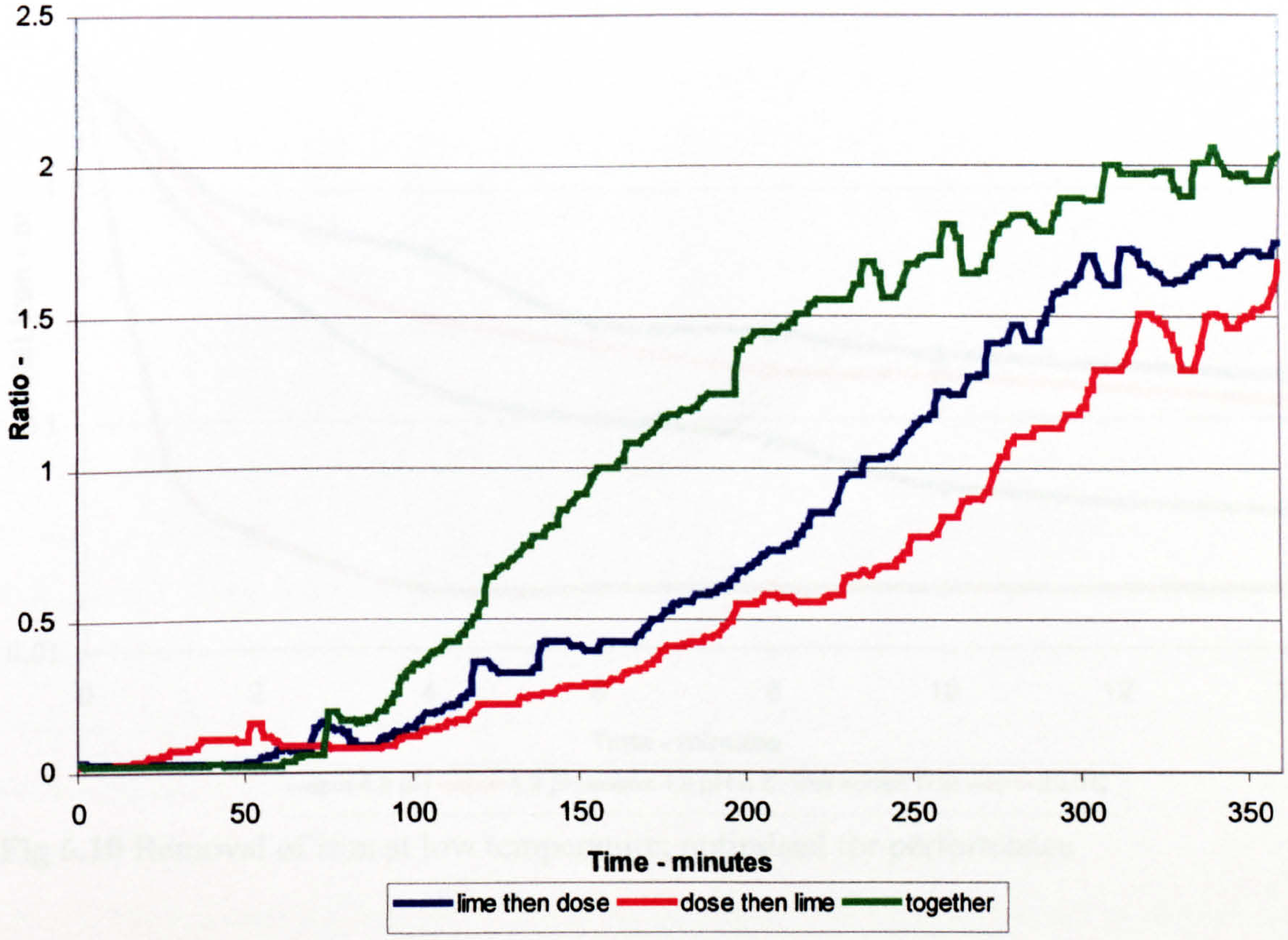


Fig 6.9 The effect of lime addition on slow mixing

As with the rapid mixing experiment, when lime is added after the coagulant, weaker smaller flocs are formed. The addition of lime and coagulant together improves the performance but the addition of lime before the addition of the coagulant is more significant when the effect on flocculation is studied. The increased floc size and strength during rapid mixing translates to a substantial quicker growth of floc during slow mixing, with a larger floc formed.

The experiments looking at the removal of iron at low temperatures all involved adding the lime and coagulant dose together. As **Fig 6.8** and **6.9** both show that lime added before coagulant significantly improves performance, it was important to repeat the iron removal experiment at low temperature and optimum pH (4.9), but with lime added before the coagulant. **Fig 6.10** shows the removal of iron at 4°C, with lime and coagulant added together, at pH 4.8 and with the pH optimised for low temperature at 4.9. The experiment was repeated with lime added before coagulant at the optimised pH; the removal of iron at 20°C (**Fig 6.2**), for comparison

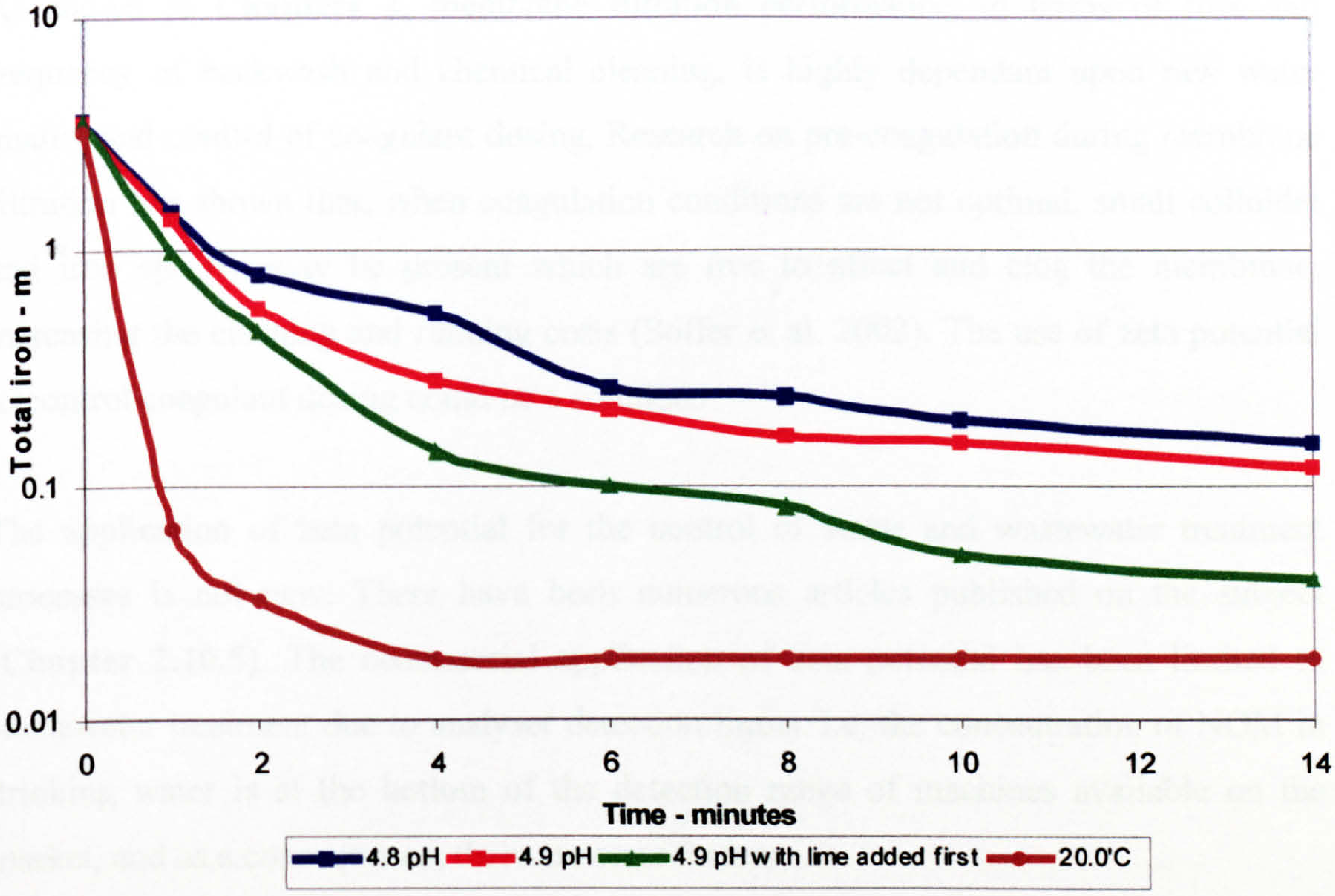


Fig 6.10 Removal of iron at low temperature; optimised for performance

The results show that the removal of iron at low water temperatures, when lime and coagulant are added together, is improved when the pH is increased to 4.9. However, the improvement is slight with over 0.12mg/l Fe^{3+} still remaining in solution. When lime is added before the coagulant, the greater floc growth increases the removal of excess iron through enmeshment by the larger floc, with only 0.04mg/l Fe^{3+} left in solution. It should be noted that 14 minutes of mixing is required to achieve this level, which would not be a problem with normal clarifier treatment where the residence time can be over 30 minutes.

However the optimisation of the coagulation process is this report is designed for the use of a pre-coagulation stage upfront of an ultrafiltration membrane. A benefit of combining coagulation and ultrafiltration membranes, over normal clarification, is process intensification; however, if over 14 minutes residence time is required for the removal of iron during coagulation at low temperatures, then this benefit is void.

6.3.5 Zeta potential for coagulant control

As shown in **Chapters 2**, membrane filtration performance, in terms of flux and frequency of backwash and chemical cleaning, is highly dependant upon raw water quality and control of coagulant dosing. Research on pre-coagulation during membrane filtration has shown that, when coagulation conditions are not optimal, small colloidal and iron species may be present which are free to affect and clog the membrane, increasing the cleaning and running costs (Soffer et al. 2002). The use of zeta potential to control coagulant dosing could be a solution.

The application of zeta potential for the control of water and wastewater treatment processes is not new. There have been numerous articles published on the subject **(Chapter 2.10.5)**. The commercial application of zeta potential has been limited to wastewater treatment due to analyser detection limits. I.e. the concentration of NOM in drinking water is at the bottom of the detection range of machines available on the market, and as a consequence, there are error factors.

This investigation into zeta potential is to determine where in the process stream the optimum position of the sensor is, and secondly can a zeta potential analyser give reliable measurements in an in-line process stream of water with relatively low levels of NOM.

Lab based experiments were conducted to investigate the optimum position to place the zeta potential sensor during the mixing process. **Fig 6.11** shows the changes to ZP during the mixing process. In this experiment one minute of rapid mixing was followed by a period of slow mixing. Excess coagulant was added to highlight the changes to ZP

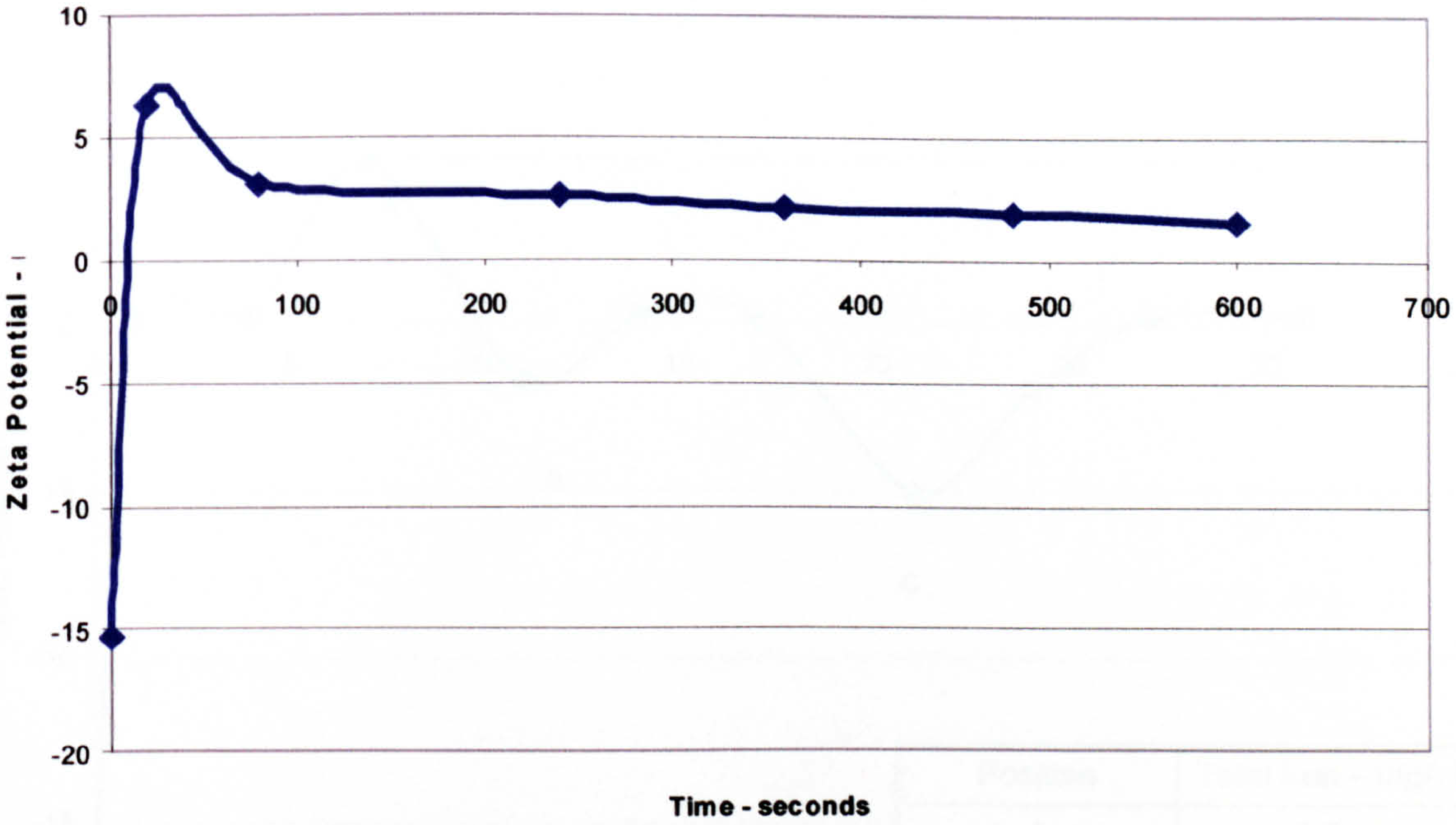
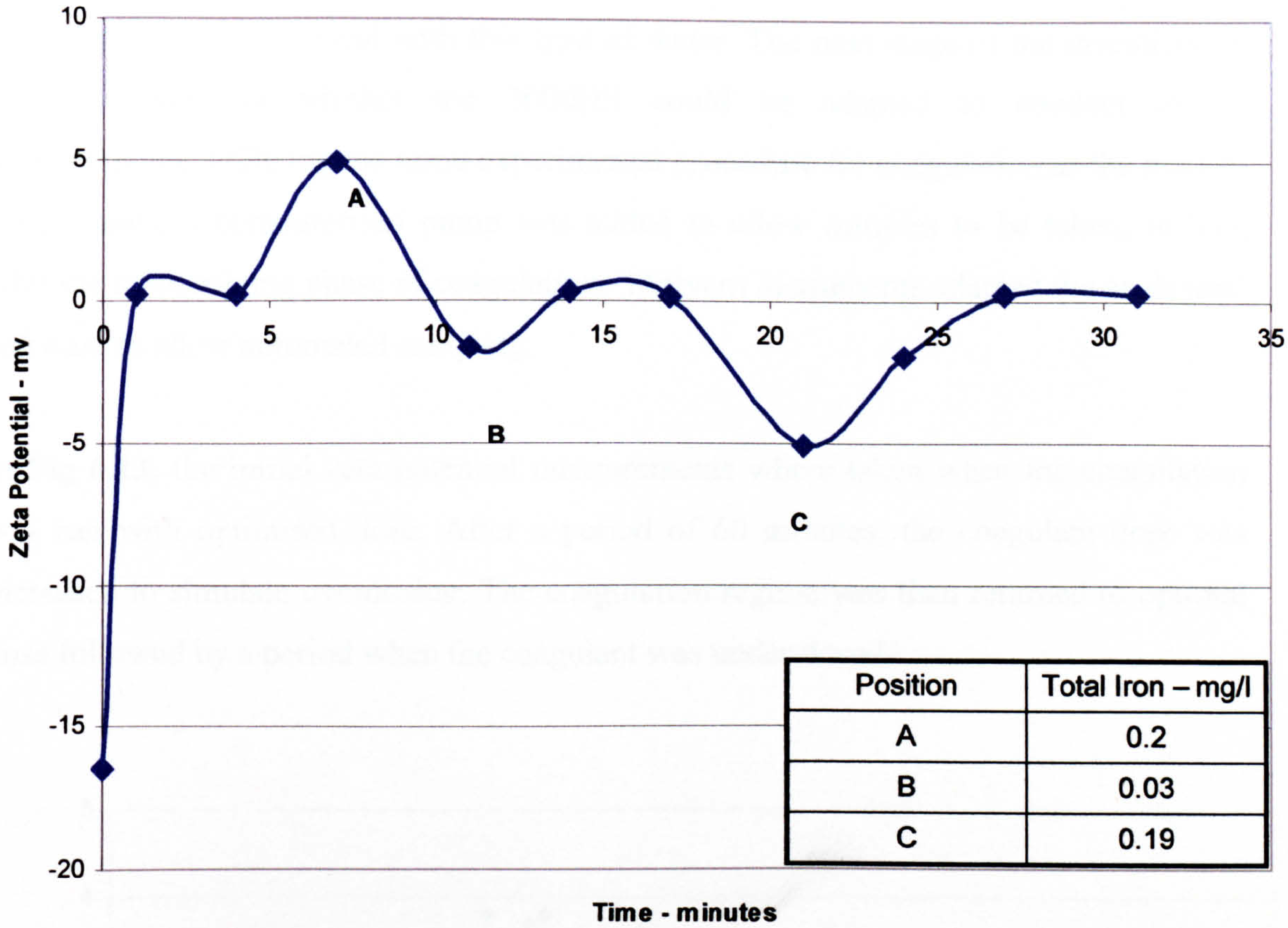


Fig 6.11 The changes to zeta potential during the mixing process

The addition of coagulant changes the zeta potential from –16mv to +5mv (indication of slight overdosing). The dispersion of the ferric ions and formation of pin flocs reduces the ZP during rapid mixing. Thereafter the zeta potential is relatively stable with a gradual reduction due to enmeshment of the excess iron. This result indicates that positioning the sensor after rapid mixing would be suitable

Lab based experiments were conducted with varying levels of natural organic matter at fixed coagulant dose, to see if the Malvern 3000HS could detect changes in zeta potential with relatively low levels of NOM. Raw water with a known NOM content was initially used and periodically throughout the experiment the water supply was changed to waters containing different NOM levels. **Fig 6.12** shows the changes to ZP when inlet water conditions changed. Samples were taken manually from the coagulation process after rapid mixing and injected into the 3000HS. Samples were also taken and passed through 0.8µm filters to remove flocs and then tested for total iron levels



Position	Total Iron – mg/l
A	0.2
B	0.03
C	0.19

Fig 6.12 Effect on zeta potential by varying raw water quality and total iron levels

Addition of coagulant changes the zeta potential to near zero. A decrease in natural organic matter (NOM) content (position A) causes an increase in ZP due to excess levels of coagulant. By decreasing the coagulant dose, ZP drops back to optimum levels [B]. An increase in NOM content causes a drop in ZP values [C] requiring additional coagulant to reach optimum coagulation.

The table shows the levels of total iron at the various positions. The iron present at [A] is due to the presence of excess ferric sulphate. The reason there is iron present at [B] and [C] is due to the presence of natural iron in the feed water. At near zero ZP this iron is greatly reduced. This graph and table show that both under and overdosing can lead to excess iron in solution.

The results from the manual analysis show that the Malvern 3000HS can deal with the solid concentrations typical with this type of water. The next stage of the investigation was to determine whither the 3000HS could be adapted to conduct in-line measurements. Utilising the same experimental procedure for coagulation as the manual experiments, a computerised pump was added to allow samples to be taken, in-line, after the rapid mixing phase of coagulation. Malvern instruments adapted the analysers' software to allow automated sampling.

In **Fig 6.13**, the initial zeta potential measurements where taken when the coagulation was run with optimised dose. After a period of 60 minutes, the coagulant dose was increased to simulate overdosing. The coagulation regime was then returned to optimal dose followed by a period when the coagulant was under dosed.

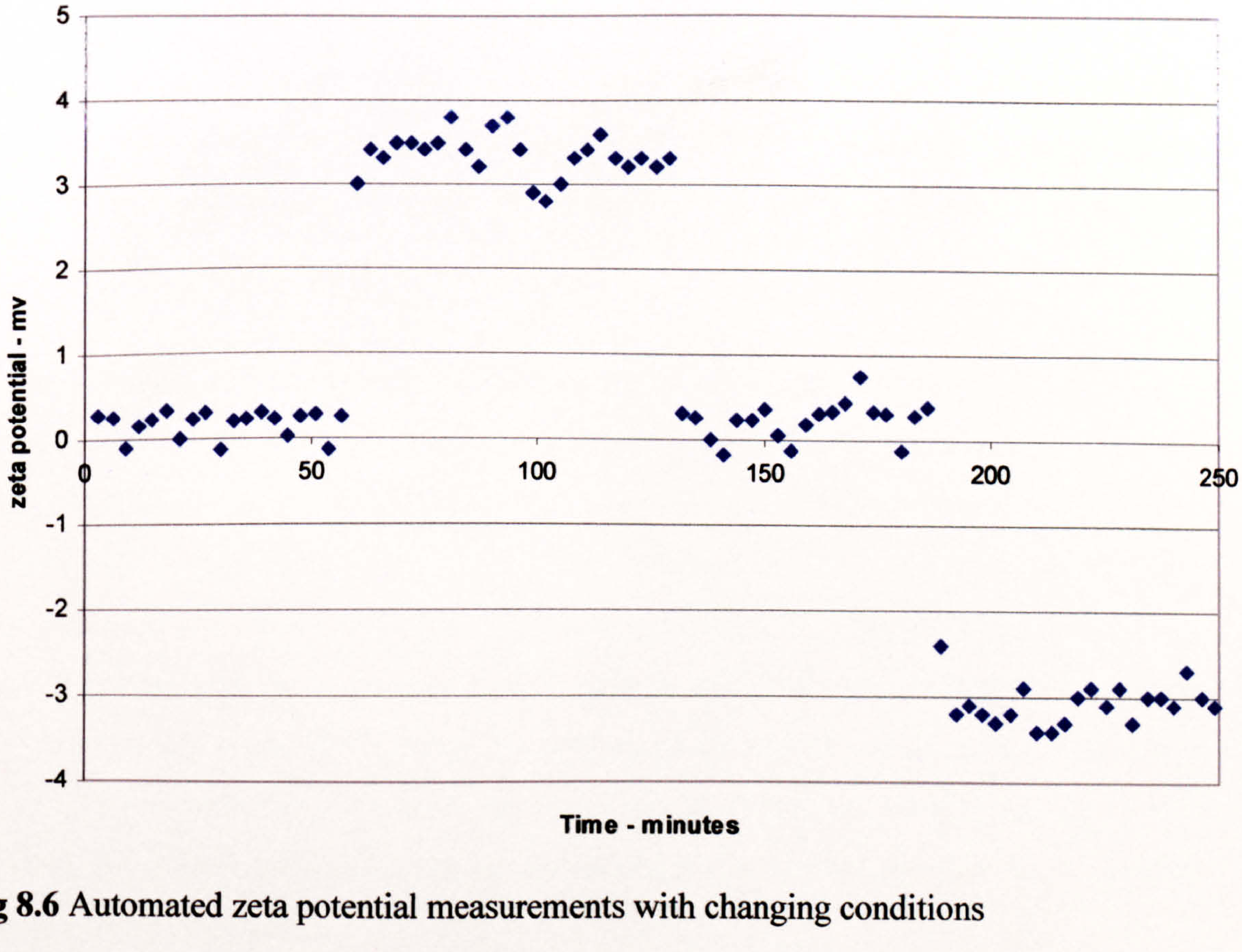


Fig 8.6 Automated zeta potential measurements with changing conditions

The results show that the automated zeta potential measurements can detect changes in coagulation conditions and produce consistent results. The variation in measurements for all conditions was only ± 0.7 mv. As the residence time during rapid mixing was only 1 minute, the 3-minute interval between zeta potential measurements was more than adequate to detect major changes in conditions

With the aid of Malvern Instruments the use of zeta potential as an in-line coagulant dosing control has been verified, albeit for this type of water and ferric sulphate. It should be noted that, although, in the experiments discussed here the optimal dose corresponded to near zero zeta potential, there may be conditions where that may not be the case. A negatively charged solution may be better suited to filtration by a negatively charged membrane, whereby charge repulsion decreases the levels of membrane fouling. Further research is required.

6.4 Conclusions

As already mentioned, the role of coagulation combined with membrane filtration has seen increased interest. As this thesis is based on the impact pre-coagulation has on ultrafiltration membrane performance, the optimisation of coagulation conditions in this chapter, represents the conditions that provide the greatest removal of NOM in the shortest possible time, while allowing the flocs to grow large enough to remove any excess iron, particularly during periods of cold temperature.

The results for optimising the pH are in accordance of published literature. Adin A. et al., (1998) showed that for ferric ions, the predominant coagulation of adsorption and charge neutralisation occurs between pH 3 – 5. Alum on the other hand performs best at pH 6 – 7, the predominant coagulation mechanism being sweep or adsorption of micro-flocs. The experiments in this chapter show that although flocs are produced over the range of pH values, there is a significant improvement in performance at the optimum pH. The results show that for ferric sulphate, the optimum pH value for coagulation was 4.8; for ferric chloride the optimum pH value was 5.0; and for alum the optimum pH value was 6.7.

At the optimum pH, the amount of coagulant available greatly affects the coagulation performance As the optimum coagulant dose is generally associated with a near zero zeta potential, the results indicate that when each coagulant is operated at its optimum, ferric sulphate outperforms both ferric chloride and alum. The difference between the two ferric salts is slight, with ferric sulphate producing the largest, most stable floc. Alum performs poorly, with more than double the mass of coagulant needed to reach the performance of the ferric salts. The difference in treated water quality, with ferric coagulants outperforming alum, is again shown in literature. Volk C et al., (2000) showed that at lower pH, ferric coagulants performed generally better for the removal of organic carbon than alum.

Manipulation of the mixing regime during orthokinetic flocculation allows control of the final floc size. By increasing the initial rapid mixing speed, the rate of growth during the slow mixing period is affected. A high shear rate ($447s^{-1}$) induces greater particle collision and micro-floc formation, allowing an increased rate of growth during slow mixing. However, at the higher shear rate, all the coagulant is dispersed and formed into flocs, which are larger than 8 microns, after 60 seconds of rapid mixing, which is sufficient to removal the coagulated NOM. This result is similar to that published by Judd and Hillis (2001) who indicated that the flocs need only growth to around 2μm and can be reached with only 30 seconds of rapid mixing, as relating to NOM removal.

It should be noted that although the majority of the NOM is removed, there still remained a small fraction in treated water. Analysis of the raw water **(Chapter 5.3)** showed that it contained hydrophilic and hydrophobic neutrals, which Pikkarainen et al (2004) showed were not removed by coagulation.

However, as the raw water contains species other than NOM, in particular colloidal and dissolved iron, and ferric sulphate is used as the coagulant, it was important to study the removal of iron during the mixing process. This is important; as colloidal iron has been shown to affect and clog membranes (Gabelich C. J. et al., 2002) The research showed that when ferric sulphate was used as the coagulant there remained residual iron after the period of rapid mixing, therefore a period of slow mixing is required to increase the size of flocs and remove the remaining iron by enmeshment in the growing flocs. the time required to remove the iron at 20°C, is 3 minutes.

There are several variables that affect this slow mixing time. Firstly excess coagulant, there is a maximum number of flocs formed by precipitation of iron hydroxide at any given shear rate, therefore overdosing with coagulant will leave excess iron in solution, and as a consequence the problem of removing excess iron through enmeshment would be exacerbated, and hence the effect on the membrane would increase. Secondly temperature, as the temperature decreases, so to does the flocculation performance. A lower temperature causes the formation of smaller and denser flocs. The reduced size of the flocs diminishes the performance of 'sweep flocculation', as there is a reduced surface area to enmesh the particles. This has a significant impact on the removal of the excess iron fraction.

Results show that the initial coagulation process is not greatly affected by temperature; however, temperature does affect the rate of flocculation. At 20.0°C the excess iron is removed by enmeshment after 4 minutes. As temperature falls so the time required to remove the iron increases. At 4°C iron remains in solution even after 14 minutes.

Changing the solution chemistry can reduce this problem. The results show that the optimum pH of coagulation with ferric sulphate at 4°C shifts towards alkalinity by 0.1 pH units i.e. 4.9 compared with a pH at 20°C of 4.8. This increase in pH has been shown by many researchers (see **Chapter 2.8.3**) and may be due to the effect on the precipitation and solubility of ferric sulphate at the lower temperature (Kang L. S. and Cleasby J. L., 1995).

However this change in pH only improves the removal of excess iron slightly. Further research showed that the low turbidity of the water hindered the coagulation process. Particulates in water aid coagulation as they provide nucleating sites on which flocs can form and grow. Low turbidity waters lack these seeding points and although at high temperatures this is not a problem; at low temperatures this lack of particulates can hinder the coagulation process. The addition of lime for pH correction can remedy this problem due to its colloidal nature.

There has been numerous studies on the impact lime has on coagulation, as well as debate on where in the process stream the addition of lime has the greatest impact (Gregor J. E. et al., 1997). However, the impact of lime on coagulation at low temperatures has not been fully investigated, particularly on the removal of excess iron.

The results show that the removal of iron at low water temperatures, when lime and coagulant are added together, is improved when the pH is increased to 4.9. However, the improvement is slight with over 0.12 mg/l Fe^{3+} still remaining in solution. When lime is added before the coagulant, the greater floc growth increases the removal of excess iron through enmeshment by the larger floc, with only 0.04mg/l Fe^{3+} left in solution after 14 minutes of mixing. Further research is required to determine if the removal of excess iron at low temperatures can be improved below this level.

As variations in coagulant levels can have a dramatic effect on membrane performance, control of coagulant dosing is paramount. The use of zeta potential is one solution. This investigation into zeta potential was to determine where in the process stream the optimum position of the sensor is, and secondly could a zeta potential analyser give reliable measurements in an in-line process stream of water with relatively low levels of NOM.

With the aid of Malvern Instruments the use of zeta potential as an in-line coagulant dosing control has been verified, albeit for this type of water and ferric sulphate. The results from the manual analysis show that the Malvern 3000HS can deal with the solid concentrations typical with this type of water. The results also show that the automated zeta potential measurements can detect changes in coagulation conditions and produce consistent results. The variation in measurements for all conditions was only ± 0.7 mv.

It should be noted that, although, in the experiments discussed here the optimal dose corresponded to near zero zeta potential, there may be conditions where that may not be the case. A negatively charged solution may be better suited to filtration by a negatively charged membrane, whereby charge repulsion decreases the levels of membrane fouling. Further research is required.

The optimisation of the coagulation process is this report is designed for the use of a pre-coagulation stage upfront of an ultrafiltration membrane. In summary, the research indicated that, at summer operating temperatures, the optimum pH for flocculation is 4.8. The optimum coagulant dose depends on the raw water quality and lies between 2.0 and 3.0 mg/l of Fe^{3+}. A mixing regime of 60 seconds rapid mixing (shear rate $G = 447\ s^{-1}$) followed by 3 minutes slow mixing (shear rate $G = 20\ s^{-1}$) is required for flocculation of the NOM and adequate enmeshment and removal of excess iron. How this optimised coagulation regime impacts on ultrafiltration performance is discussed in the following chapters.

Chapter 7

Pre-coagulation and ultrafiltration membranes

7.1 Introduction

In the previous chapter, the coagulation regime was optimised to reduce the levels of natural organic matter and iron in the shortest possible time. The research indicated that the optimum pH for flocculation of the NOM by ferric sulphate lies between 4.6 and 4.8. The optimum coagulant dose depends on the raw water quality and lies between 2.0 and 3.0 mg/l of Fe^{3+}. A mixing regime of 60 seconds rapid mixing (shear rate $G = 447\ s^{-1}$) followed by 3 minutes slow mixing (shear rate $G = 20\ s^{-1}$) is required for flocculation of the NOM and adequate enmeshment and removal of excess iron. As this project involves the use of a pre-coagulation stage with ultrafiltration membranes to treat upland and lowland water, the impact of optimising the coagulation process on the performance of the UF membrane was investigated. Although two types of membrane were used in the experiments, the results from each are shown separately to avoided confusion, although the similarities and differences in performance are discussed together in the conclusion.

7.2 Summary of experimental protocols

Materials and methods pertinent to this chapter were reported in **Chapter 3.5.1** of this thesis. In summary, two types of membrane were used in this research, firstly the Norit X-flow; a polyethersulfone /polyvinylpyrrolidone blend capillary hollow fibre membrane (PES/PVP membrane) with a nominal pore size of 0.04µm, a 0.7 mm inner capillary diameter, a surface area of 3.6 m^2 and a flux of 130 l/hm^2. The X-flow was chosen as it is hydrophilic in nature and is tolerant of a wide range of pH (1-13) allowing flexibility in cleaning. Secondly, a submersible Zenon ZeeWeed® hollow fibre hydrophilic ultrafiltration membrane, with a nominal pore diameter of 0.04µm, a surface area of $0.93m^2$ and flux of 27.9 l/hm^2 was used for the experiments. Water was sourced from both Bamford WTW and Draycote WTW and the coagulant used was ferric sulphate.

7.3 Results

7.3.1 Norit membrane experiments

Experiments were conducted with a Norit bench scale UF membrane unit to assess the effects of coagulation on the performance of the membrane. To provide a base line for comparison with different mixing regimes, raw water with no coagulant was run through the membrane **(Fig. 7.1)**.

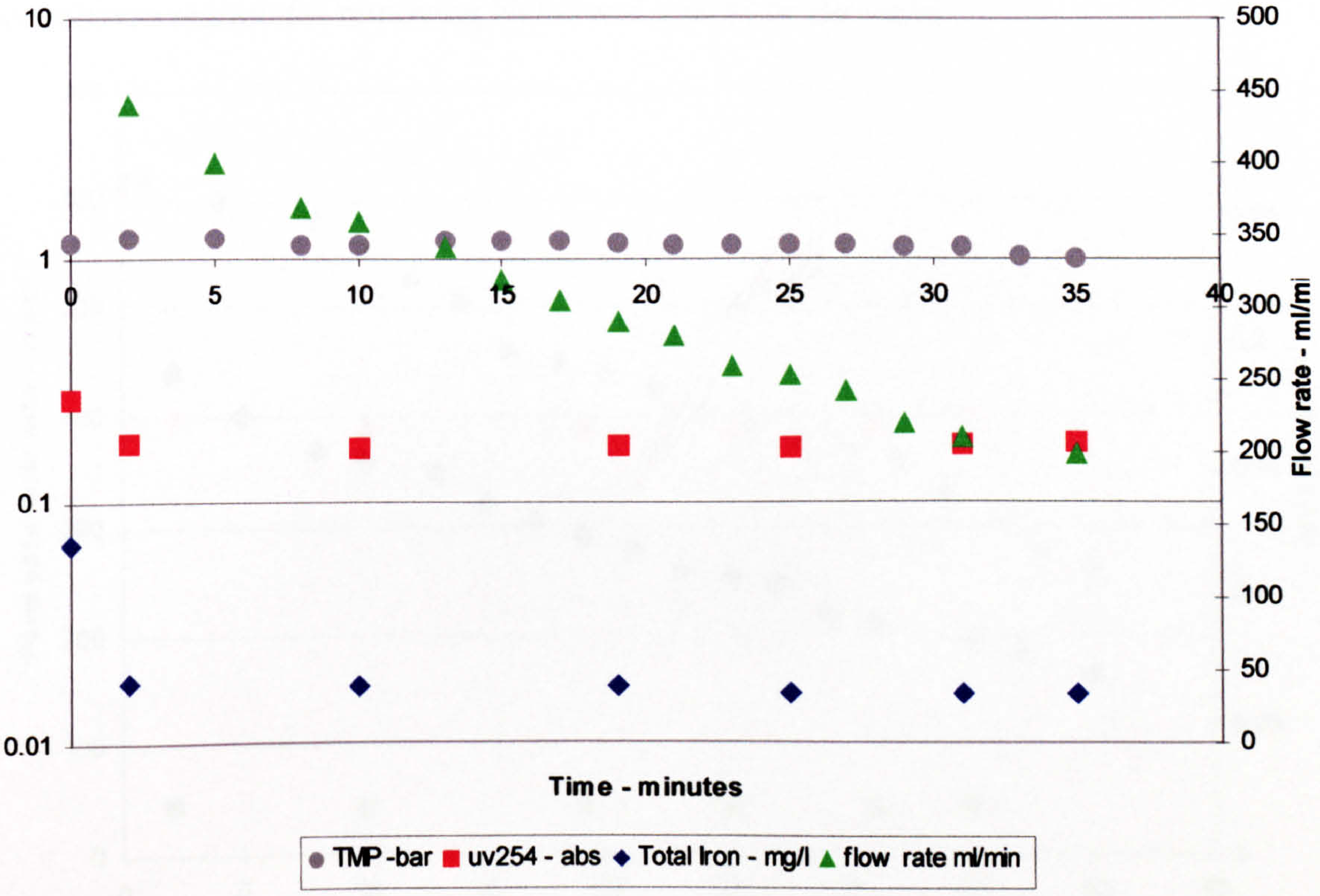


Fig. 7.1 Membrane performance without coagulant

The membrane was run with a constant transmembrane pressure, and the results show a decrease in flow-rate due to fouling of the membrane. Analysis of the raw water **(Chapter 5.3)** showed there was little particulate matter in the water; the question then is what is causing the fouling. The results for total iron show that the levels decrease significantly in the permeate. A mechanism for the removal of iron is adsorption onto the membrane. Iron can be present in the water as organically bound iron, and this may explain why NOM and Iron levels are reduced simultaneously. The levels of UV 254 decreased, indicating that some NOM was absorbed onto the membrane surface; however, as there were significant levels of organic content in the permeate (66%) and the nominal pore size of the membrane was 0.04μm, the majority of the NOM present in the water was dissolved organics, which cannot be removed by membrane filtration alone.

Fig 7.2 shows the improved membrane performance with a coagulation stage, which involved raw water coagulated with 3 mg/l Fe^{3+} at pH 4.8, with rapid mixing for 1 minute at 250 rpm (shear rate G = 447 s^{-1}) followed by slow mixing at 30 rpm (shear rate G = $20s^{-1}$) for 4 minutes. This was previously shown to be the optimum coagulation regime for removing NOM and iron from the water.

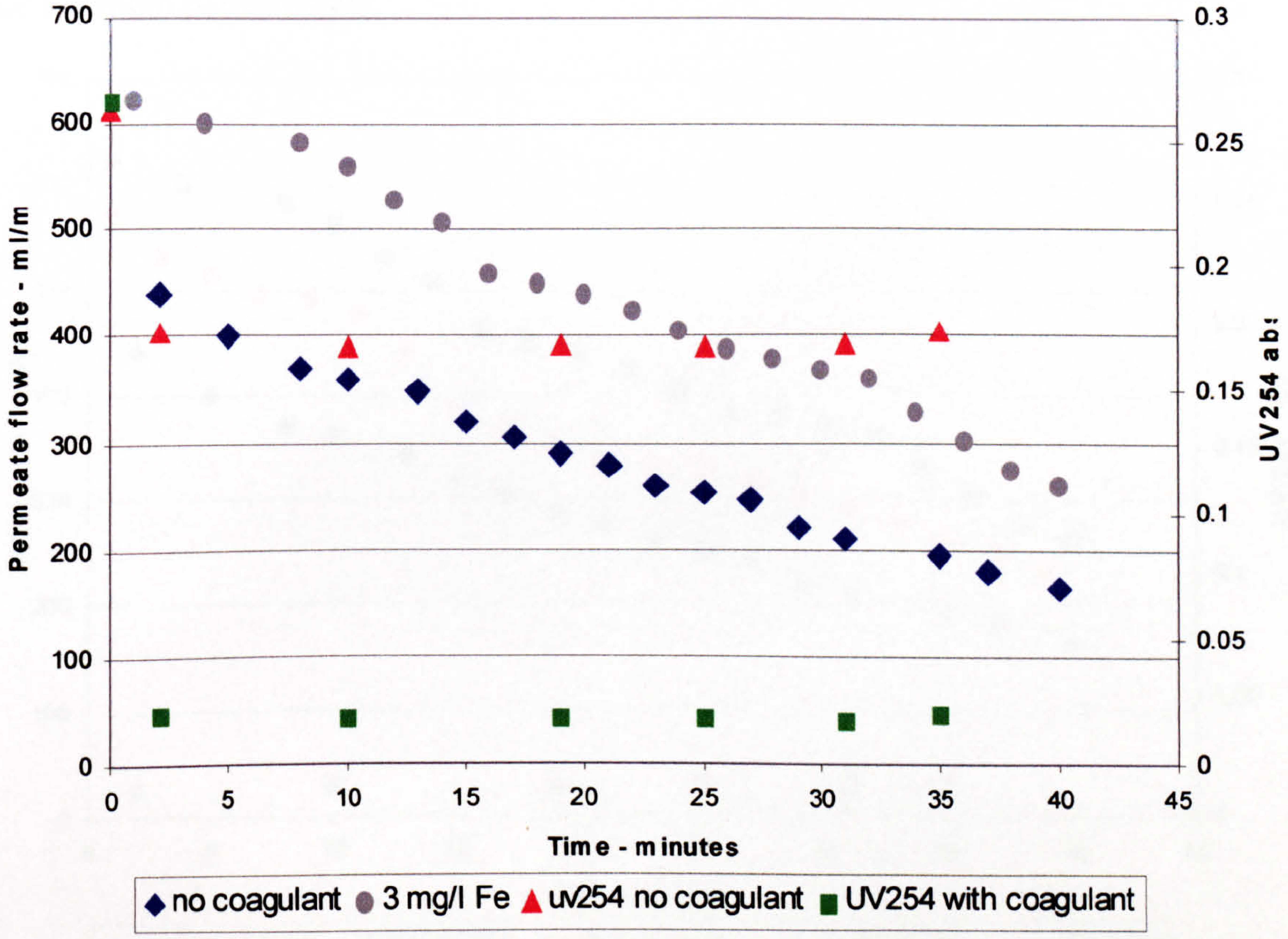


Fig 7.2 The effect of coagulation on membrane performance

The results show a significant improvement in permeate quality with the addition of coagulant, as the coagulation process flocculates the dissolved organic matter, which is then removed by membrane filtration. The TOC content of the Ferric permeate was 0.1mg/l. This is significant, as coagulation reduces the TOC to 0.3 mg/l (**Chapter 6, Fig. 6.16**). This indicates that the combined coagulation and membrane filtration process removes a fraction of the organic neutrals, which are not removed by coagulation. As the membrane is run in dead end mode and all the flocs are retained, it is difficult to speculate whither this organic reduction is due to entrapment by the floc cake or by the membrane, although it is likely that both mechanisms occur.

Although permeate quality and membrane flow rate is improved with coagulation, the rate of decrease in coagulated flow rate is such that there is still significant membrane fouling, requiring backwashing and cleaning

Research was also conducted into the use of alum as a coagulant, to determine if the flocs produced during alum coagulation are better suited for membrane filtration (**Fig. 7.3**). Results from PDA experiments indicated an alum dose of 5 mg/l at a pH of 6.1 for optimum performance.

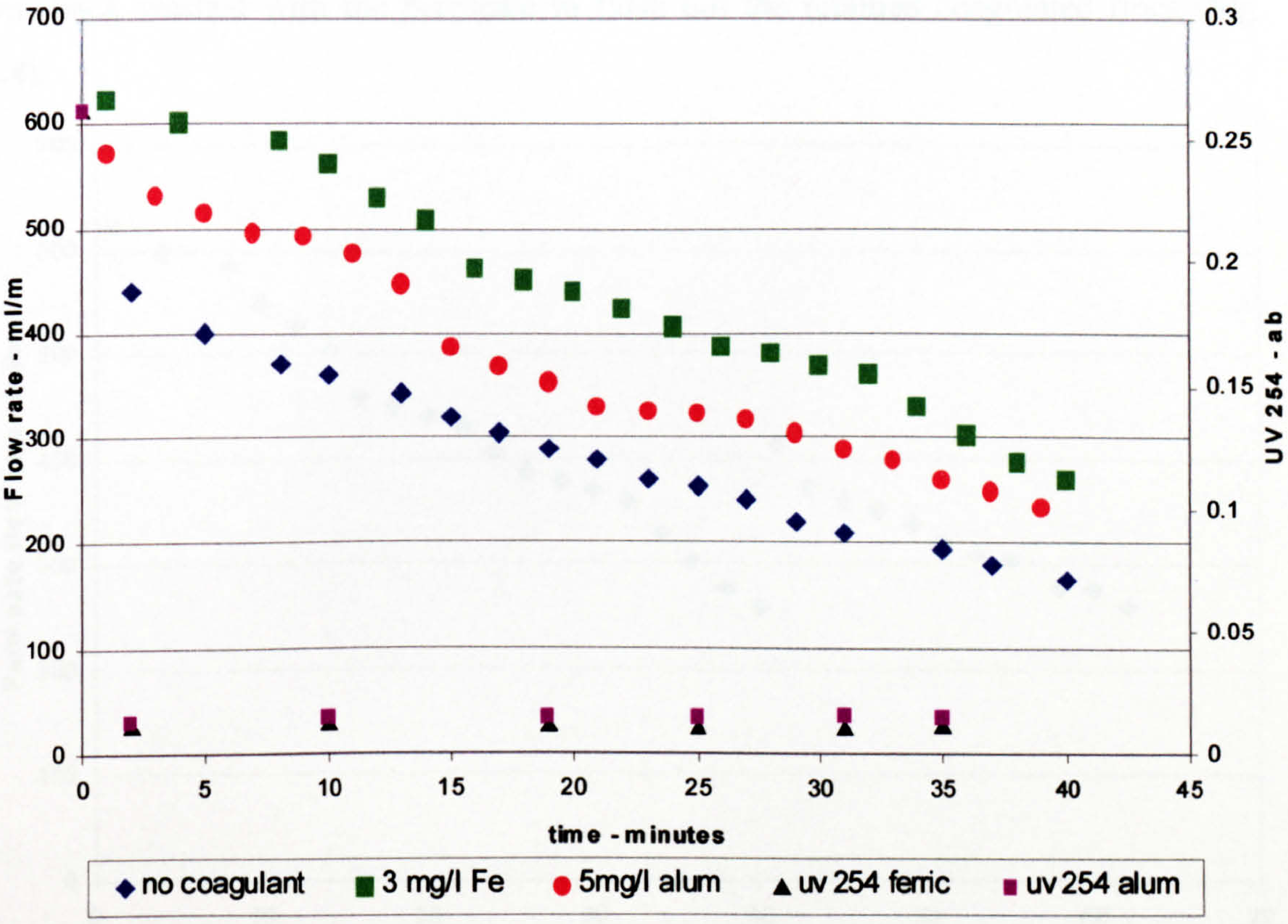


Fig 7.3 effect of different coagulant on membrane performance

By comparing the alum with the ferric sulphate, the results clearly indicate that for the water and type of membrane used, ferric is the preferred coagulant in terms of performance. Although the permeate quality with ferric and alum is very similar (0.1 and 0.12 mg/l TOC respectively), the amount of NOM after alum coagulation is 0.36 mg/l TOC (**Chapter 6, Fig. 6.18**) compared to 0.3 mg/l TOC after ferric coagulation. This indicates that there is a greater amount of uncoagulated NOM removed by the membrane with the use of alum, which may increase the membrane fouling rate.

The reduction in membrane performance may also be due to the size of the flocs blocking the inside of the membrane fibres. Coagulation with alum produces a larger; less dense floc than with ferric coagulation and it could be this increased floc size is blocking the internal fibres.

However, as filtration with dead end mode steadily retains all flocs to be filtered and will eventually lead to complete tube blockage, it could be that the length of time the experiment ran led to the flocs blocking the membrane, eventually leading to the decrease in performance. To further investigate the fouling mechanism, the membrane was back washed with the permeate to flush out the retained coagulated flocs (**Fig 7.4**).

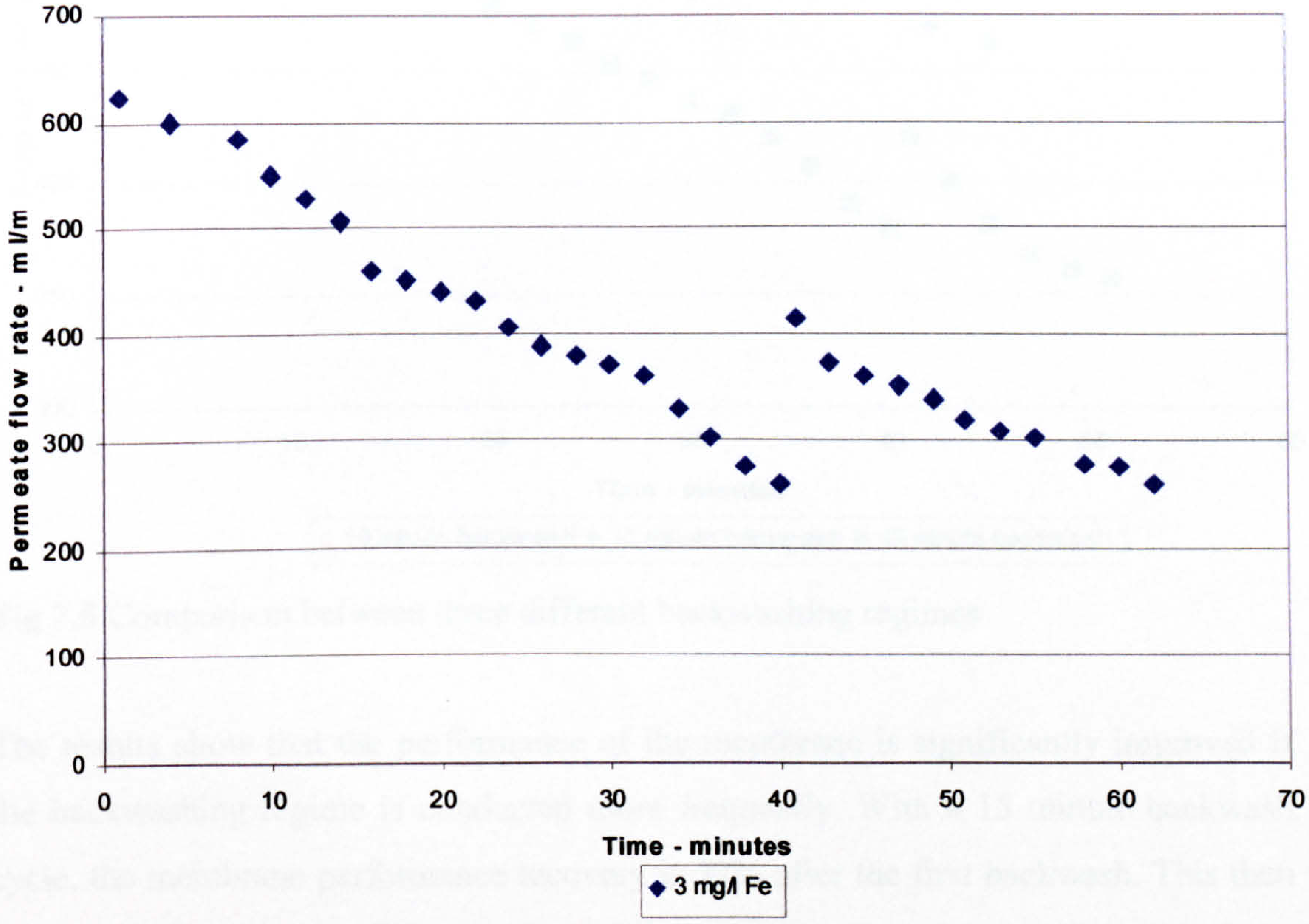


Fig 7.4 Membrane performance with backwash

The results show that backwashing, after 40 minutes filtration and for one minute, only recovers the membrane performance by 43%, indicating significant fouling remains. Since the flocs are pumped into the membrane fibres at pressure it is possible that the flocs are being compressed against the end of the membrane fibre to such an extent that backwashing at a lower pressure (as determined by Norit operating parameters) does not remove the majority of the flocs. This leads to the membrane performance deteriorating rapidly with the continued addition of more flocs.

To determine if the length of membrane run before backwashing was the main fouling factor, the experiment was repeated with a backwash after every 10 minutes and every 15 minutes (**Fig 7.5**).

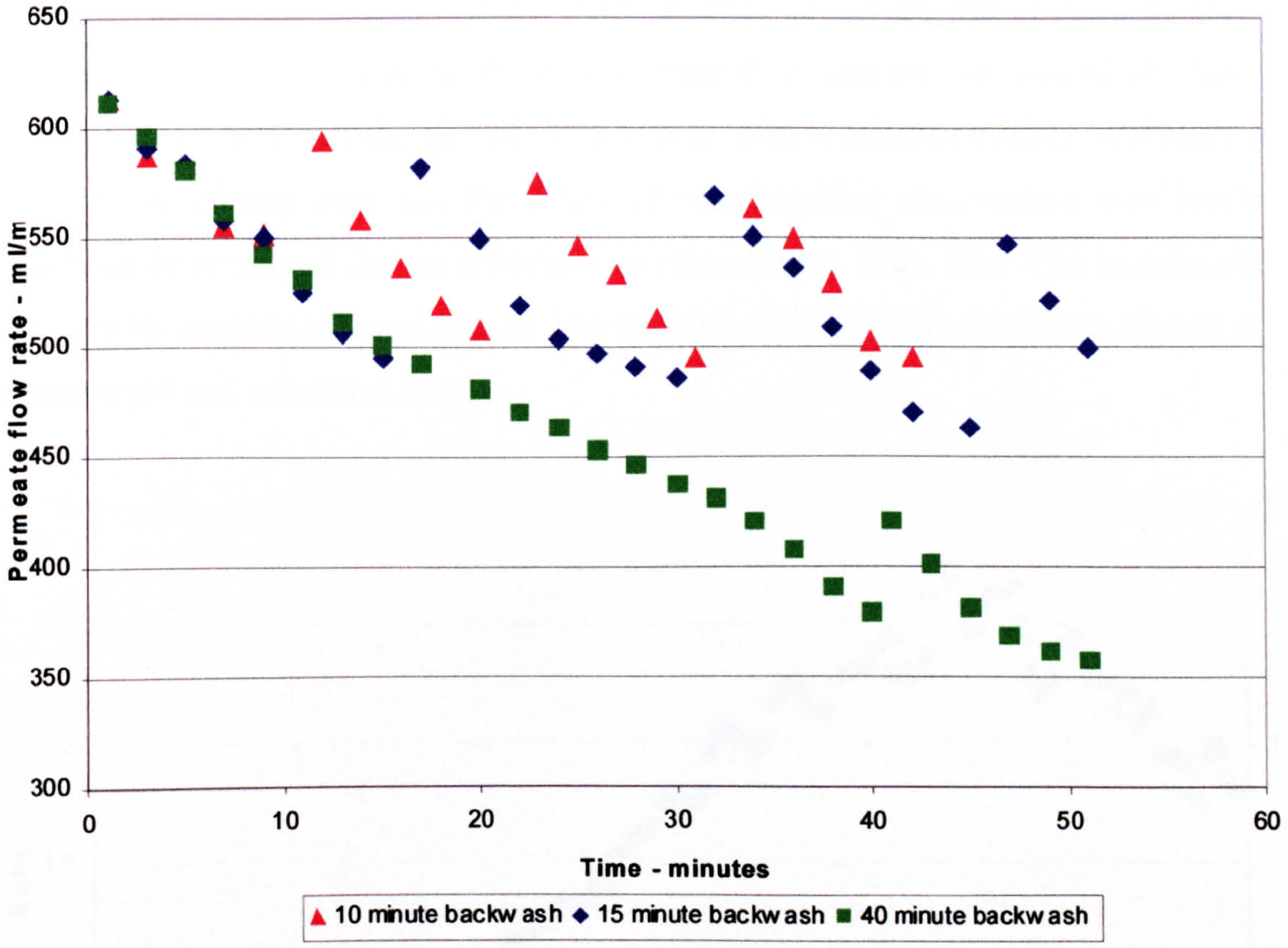


Fig 7.5 Comparison between three different backwashing regimes

The results show that the performance of the membrane is significantly improved if the backwashing regime is conducted more frequently. With a 15 minute backwash cycle, the membrane performance recovery is 72% after the first backwash. This then drops to 65% and then 54% after subsequent backwash cycles. Although this is an improvement over a 40 minute backwash cycle, there is still fouling occurring. Experiments conducted with a 10 minute cycle showed that there was no further improvement in performance with an even shorter run time, indicating that a factor other than backwash is required to reduce the membrane fouling.

Bearing in mind the mixing time required for the optimum coagulation regime, the size of flocs formed is an important factor. Visual observation confirmed that the large flocs formed by the optimum coagulant regime were blocking the hollow fibre tube (internal diameter 0.8mm), resulting in a steady reduction of permeate flow. To solve this problem of tube blocking, reducing the slow mixing time from 4 minutes to 2 minutes altered the mixing regime. PDA analysis on the growth of flocs by slow mixing shows that by reducing the mixing time to 2 minutes the size of the flocs formed are virtually half the size of flocs formed with 4 minutes mixing. Although a reduction in mixing time has the effect of reducing floc size, excess iron levels consequently increased due to reduction in enmeshment (**Fig. 7.6**). The experiment involved 60 seconds of rapid mix at 250 rpm followed by slow mixing at 30 rpm at optimum pH and coagulant dose.

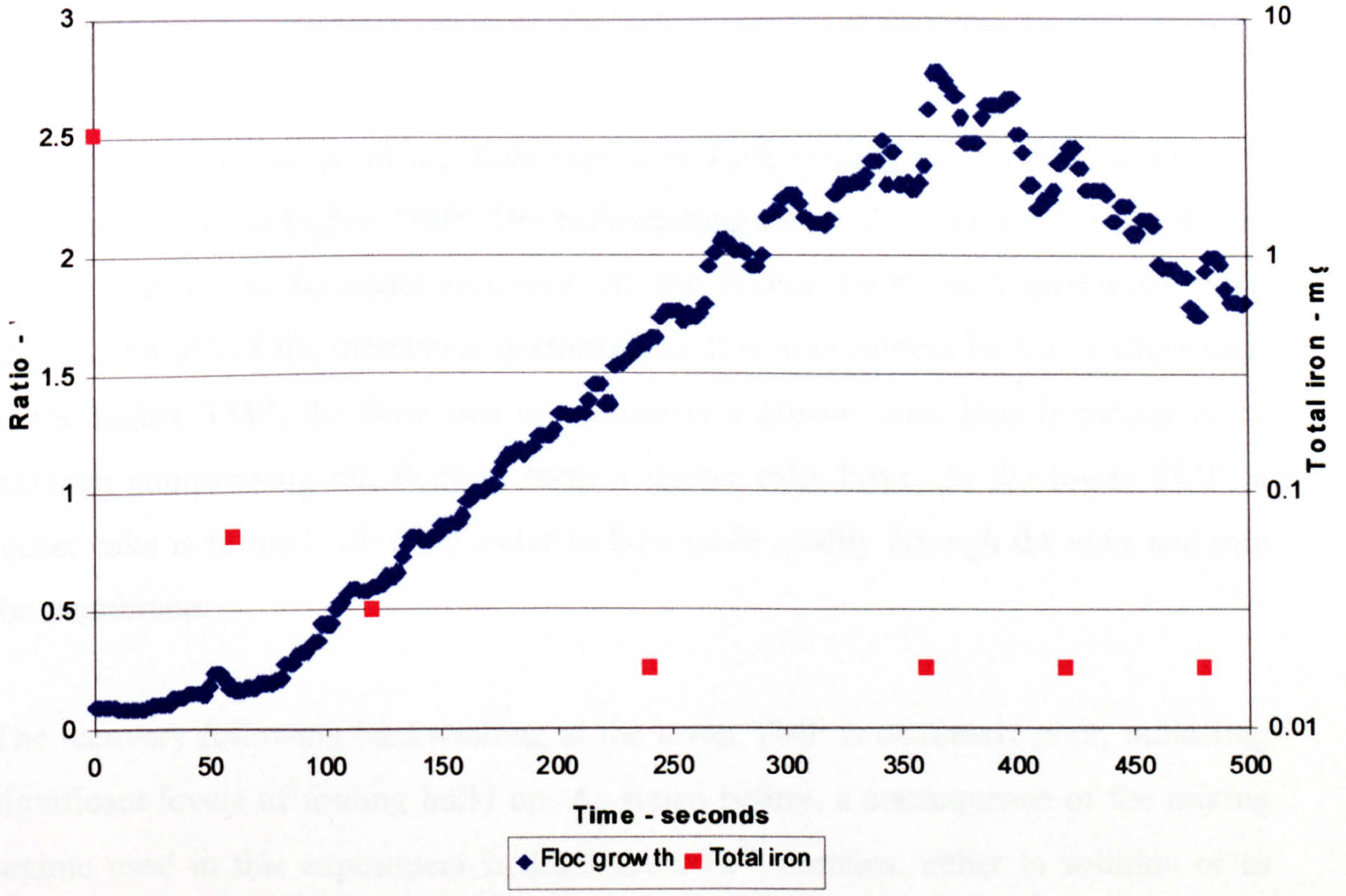


Fig. 7.6 Reduction in iron levels with one minute of rapid mixing followed by a period of slow mixing

Experiments were conducted with the revised mixing regime (2 minutes slow mixing) at two different TMPs. A backwashing regime, with a 15 minute cycle, was implemented to investigate the level of non-recoverable membrane fouling; this is indicated by the recovery of the permeate flow rate after backwashing (**Fig. 7.7**).

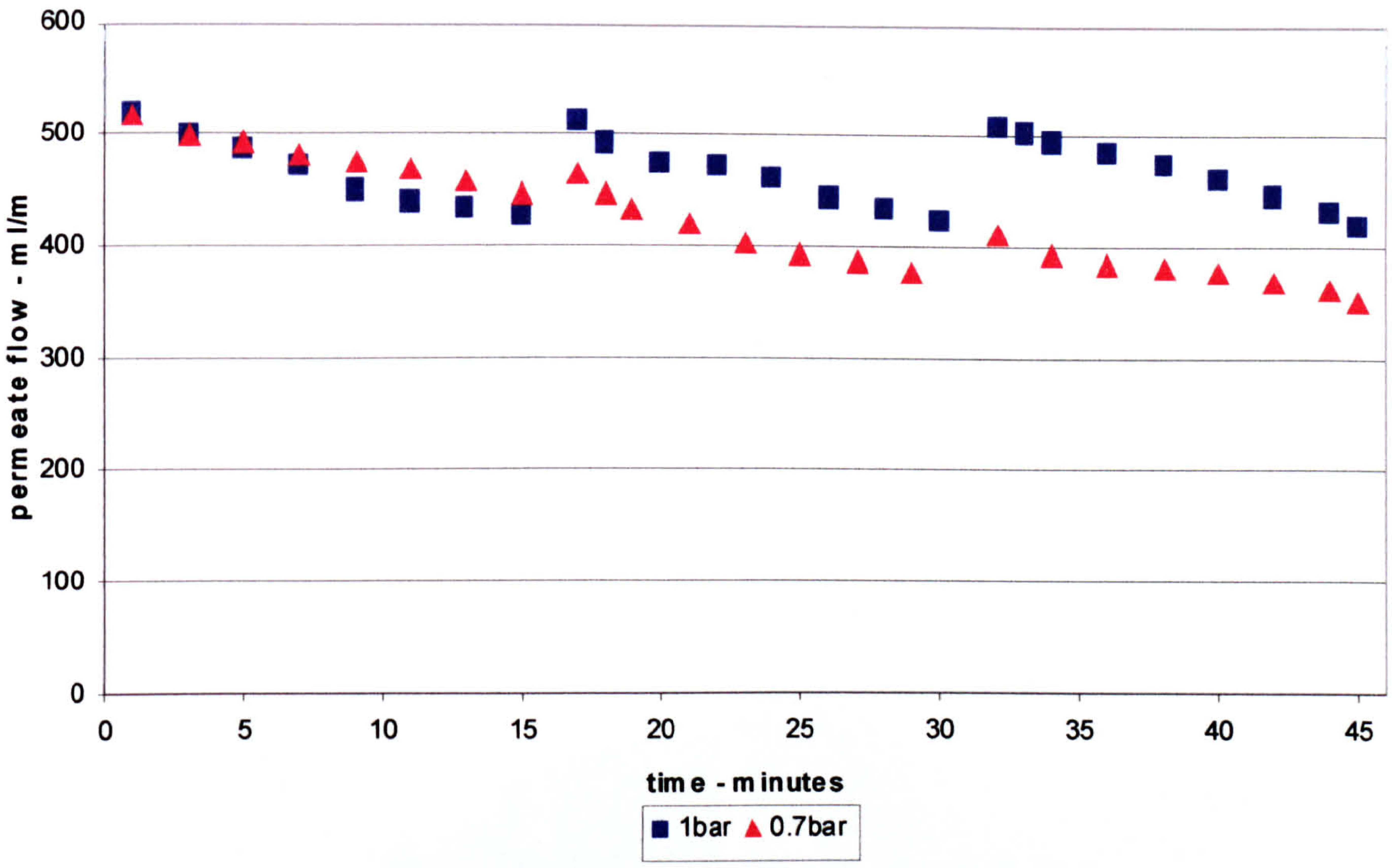


Fig. 7.7 Membrane performance at two operating pressures, including backwashing

The recovery of the permeate flow-rate after backwashing clearly shows the best performance at the higher TMP. The backwashing forces the cake off the membrane surface leading to flow-rate recovery. At the higher TMP, each backwash cycle recovers 98.9% of the membrane performance. It is also evident by the gradient that, at the higher TMP, the flow rate is reduced at a greater rate. This is indicative of pressure compressing the flocs to form a tighter cake layer. At the lower TMP, a looser cake is formed, allowing water to flow more readily through the cake and into the membrane.

The recovery following backwashing at the lower TMP is extremely poor, indicating significant levels of fouling build up. As stated before, a consequence of the mixing regime used in this experiment is that excess Fe^{3+} remains, either in solution or as individual pin flocs. This iron fraction is extremely important. At the optimum mixing regime, this iron fraction would be enmeshed onto larger flocs during 'sweep flocculation'. In our case, the compressed cake at the higher TMP acts as an additional filter which traps excess iron in the form of pin-flocs (either mechanically or by 'sweeping'), and the whole cake is subsequently removed by backwashing. At the lower TMP, the looser cake is unable to filter this excess iron, which then forms a fouling layer at the membrane surface. This iron-based layer is not removed by backwashing, and consequently chemical cleaning of the membrane is required.

A scanning electron microscope (SEM) was ultilised to confirm the fouling mechanism in the lower TMP experiment above. **Fig. 7.8** shows the surface of a clean ultrafiltration membrane, while **Fig. 7.9** shows the surface of the membrane after back flushing for this experiment.

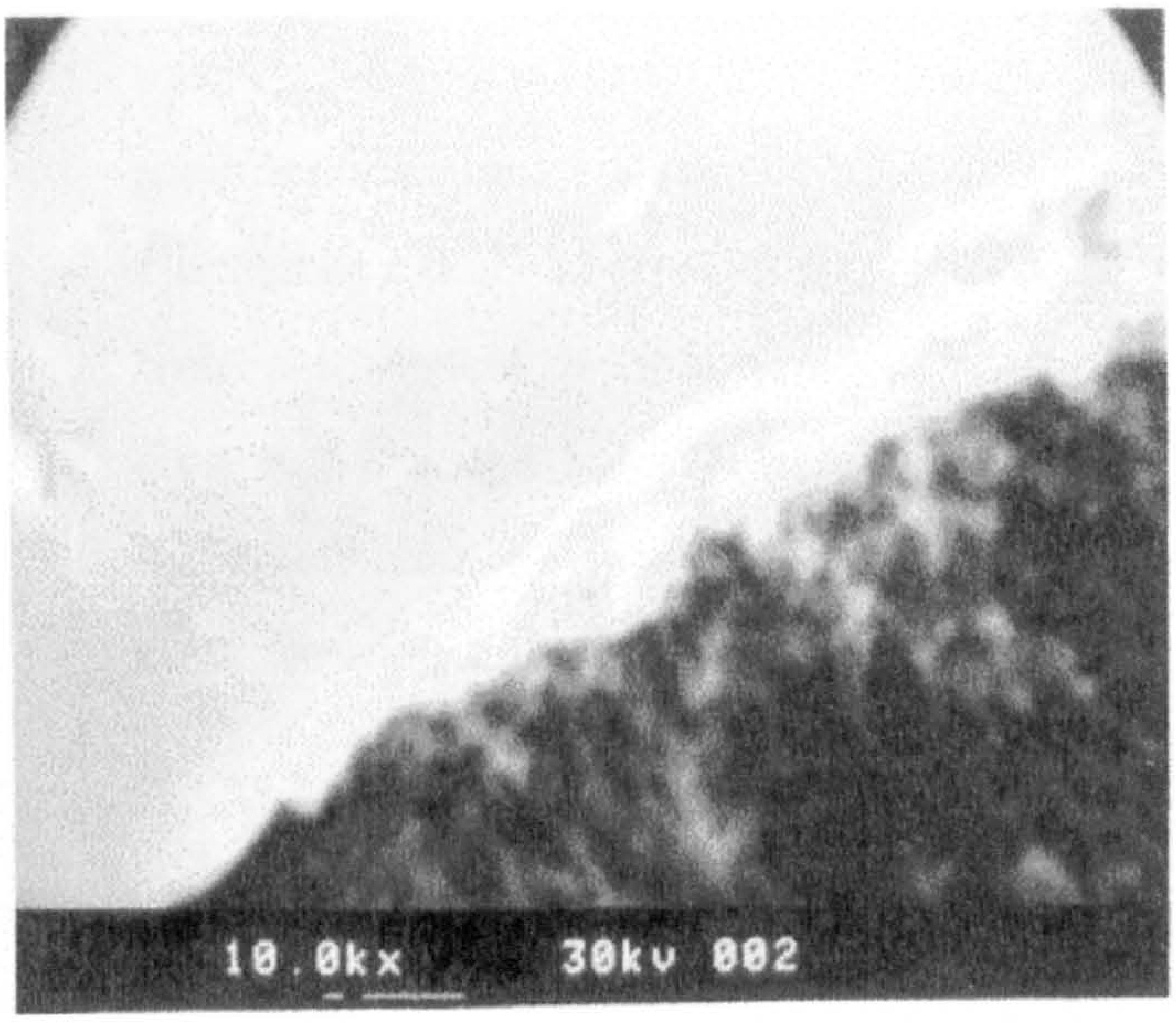


Fig 7.8 Clean membrane

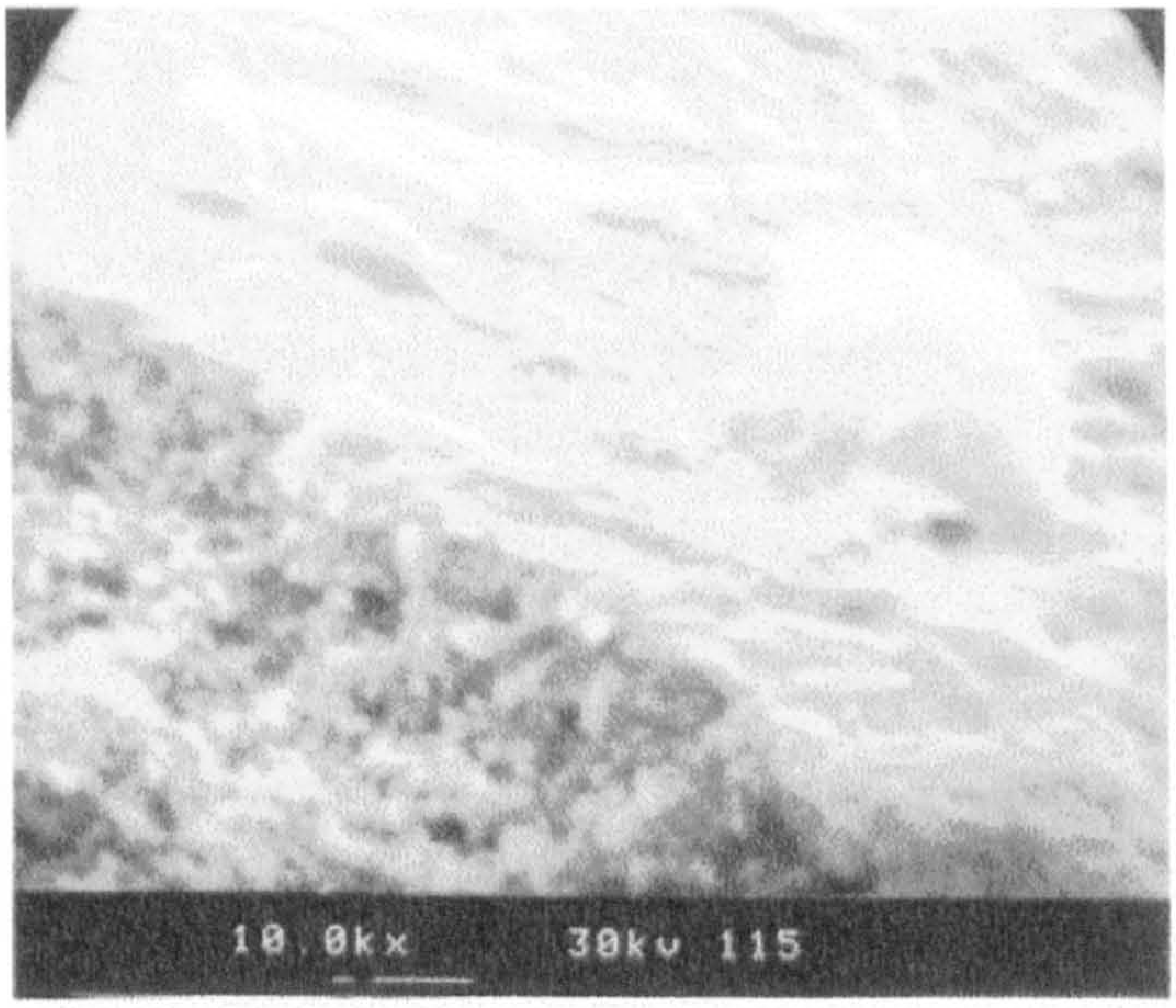


Fig 7.9 Fouled membrane

Fig. 7.9 clearly shows the surface fouling of the membrane, which may be caused by sub-micron particles of organically bound iron and pin flocs.

The results are contradictory to conventional thinking which states that a higher operating pressure will lead to a more compressed cake, which will ultimately lead to increased levels of membrane fouling. The difference in results may be due to the Norit membrane design, where the backwashing regime is able to remove the compressed cake layer more easily than a loosely formed cake layer. Visual inspection of the backwashed water seamed to confirm this. With the lower TMP, there were small amounts of flushed material, whereas with the higher TMP the backwashed water contained significant amounts of small strips of cake.

Although the higher TMP regime showed better recovery with backwashing, there was still membrane fouling occurring. To aid the determination of the fouling mechanism with the revised mixing regime, as well as with the optimum coagulation, a cleaning study was implemented.

7.3.2 Norit membrane Cleaning

To investigate the cleaning regime, the raw water, treated with 3 mg/l coagulant was run through the membrane, with backwash cycles until the flow rate decreased to 300 ml/min. Experiments were conducted with both coagulation mixing regimes (2 minutes and 4 minutes slow mixing). Once the membrane had been fouled, the module was then soaked in a cleaning solution for 2 hours before rinsing. The chemicals used were sodium hydroxide (for removing organic material) and hydrochloric acid or citric acid (for removing inorganic material). Distilled water was then run through the membrane to achieve a recovery rate. Combinations of the hydroxide and the acids were used in series to determine if greater recovery rates could be achieved.

Fig. 7.10 shows the permeate flow rates after cleaning of the membrane used to treat water with the optimum coagulation regime.

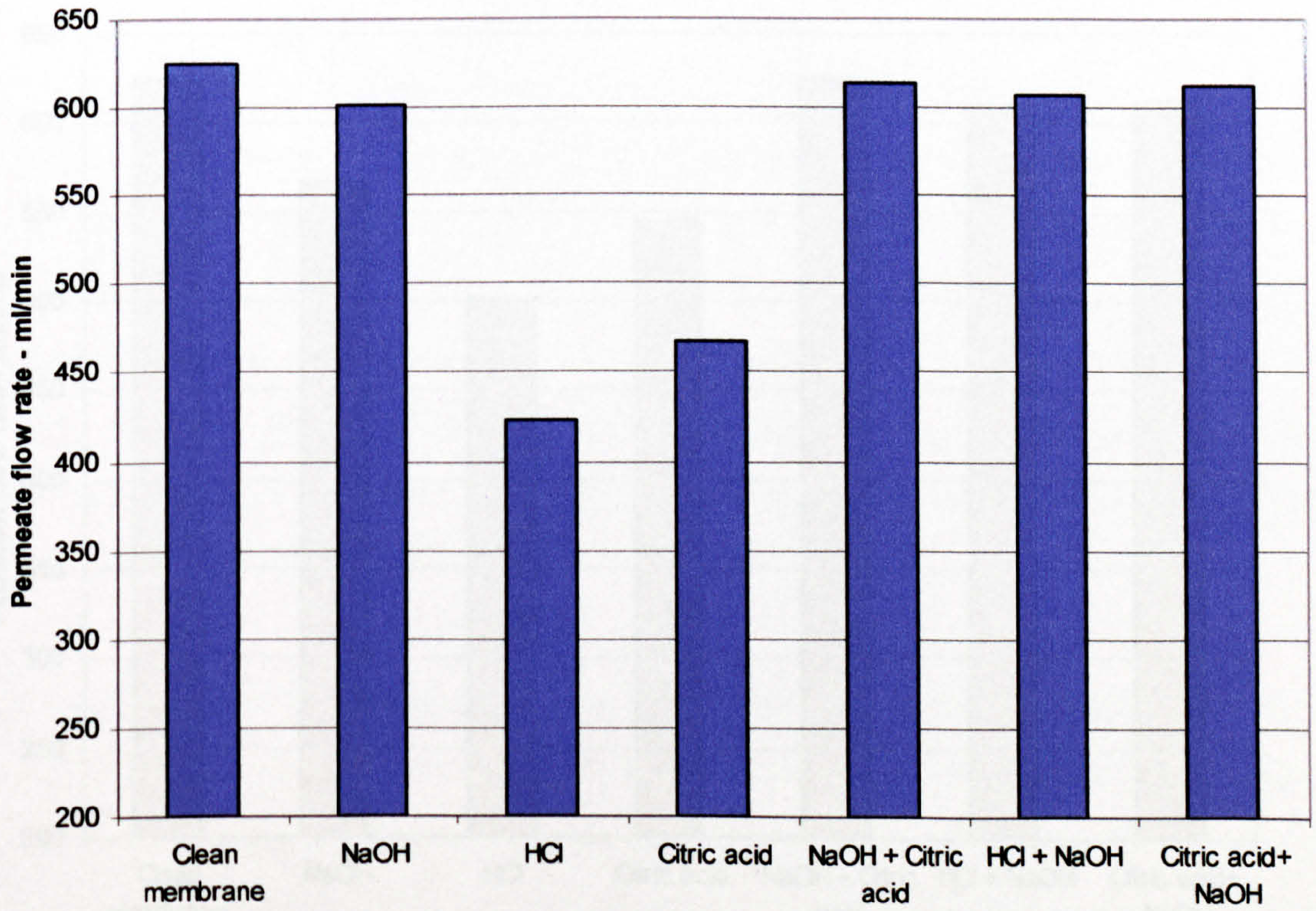


Fig 7.10 Recovery flows of optimised coagulation regime with chemical cleaning

The results show that when sodium hydroxide is used the membrane recovers 96% of its original performance. This compares favourably to the performance of hydrochloric acid (67%) and citric acid (74%) alone. When the hydroxide soak is followed by a citric acid soak, the recovery rises from 96% to 98.2%, and when the acid soaks are followed by a hydroxide soak the recovery rates rise for the hydrochloric acid to 97% and for the citric acid to 97.7%.

The results show that cleaning the membrane after the optimised coagulation requires a sodium hydroxide soak followed by an addition acid soak, with citric acid out performing hydrochloric acid. The recovery from the hydroxide soak shows that the main fouling factor is organic flocs, with some fouling from the presence of iron in the water. It is important to note that, with all the cleaning regimes the membrane was not able to achieve 100% recovery; an additional 2 hour sodium hydroxide soak was required.

Fig. 7.11 shows the permeate flow rates after cleaning of the membrane used to treat water with the revised coagulation

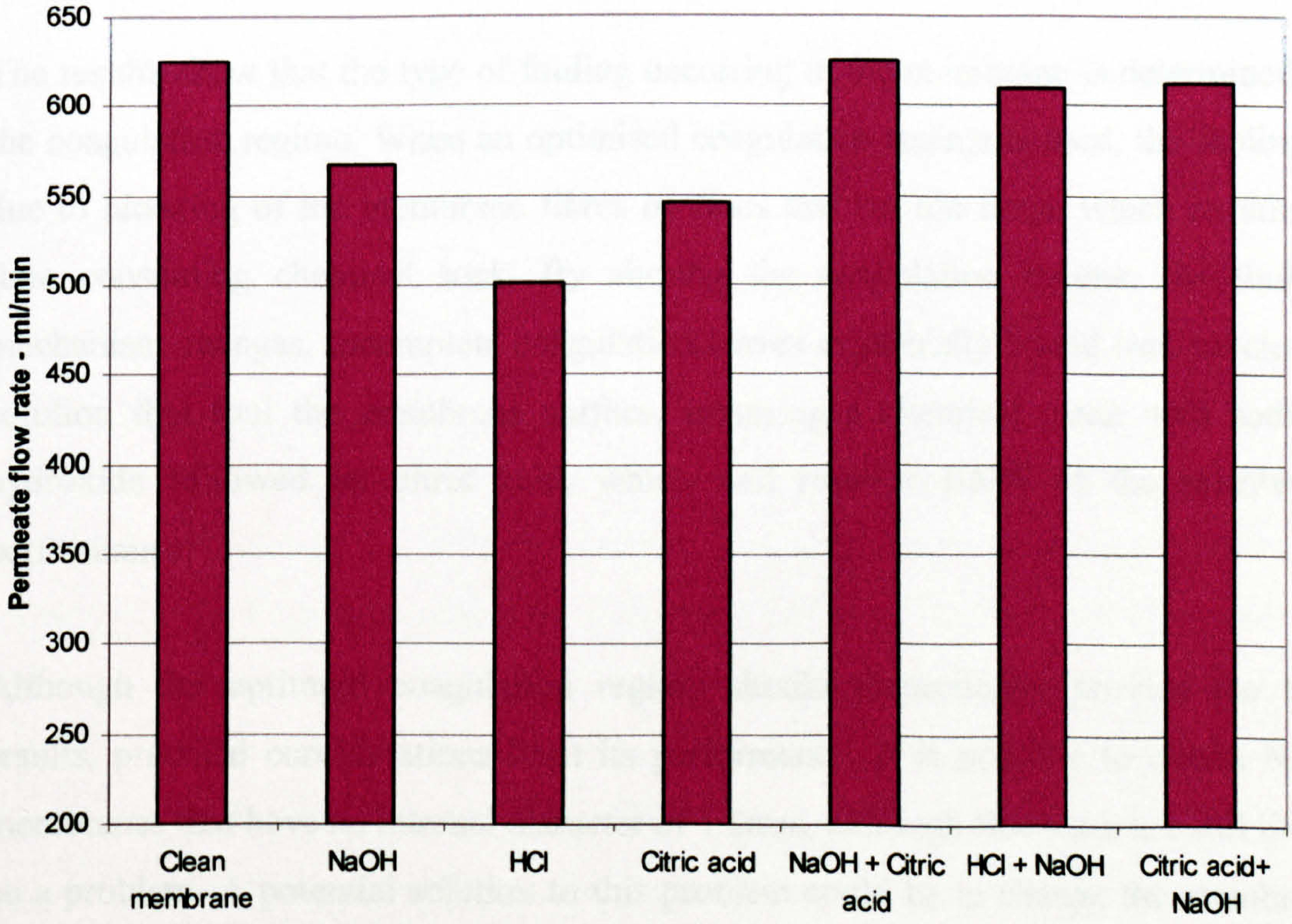


Fig. 7.11 Recovery flows of revised coagulation regime with chemical cleaning

The results show that when sodium hydroxide is used the membrane recovers 90.7% of its original performance. This again compares favourably to the performance of hydrochloric acid (80.1%) and citric acid (87.2%). When the hydroxide soak is followed by a citric acid soak the recovery rises from 90.7% to 100%, and when the acid cleans are followed by a hydroxide soak the recovery rates rise for the hydrochloric acid to 97.6% and for the citric acid to 98%.

The results show that, for cleaning the membrane after the revised coagulation, the sodium hydroxide cleaning performs less well than when cleaning the membrane used to treat water for the optimised regime. However, when the hydroxide soak is followed by a citric acid soak, the membrane recovers 100% of its performance. There is also an improved citric followed by hydrochloric acid performance, indicating that the main fouling component for the revised coagulation regime is organically-bound iron species, as opposed to fouling due to flocs blocking the membrane fibres with the optimum regime.

Both cleaning regimes show that a hydroxide soak before an acid soak is beneficial with citric acid out performing hydrochloric acid.

The results show that the type of fouling occurring in the membrane is determined by the coagulation regime. When an optimised coagulation regime is used, the fouling is due to blocking of the membrane fibres by flocs that are too large, which requires a time consuming chemical soak. By altering the coagulation regime, the fouling mechanism changes. Incomplete coagulation leaves organically bound iron species in solution that foul the membrane surface, requiring a chemical clean with sodium hydroxide followed by citric acid, which will recover 100% of the membrane performance.

Although the optimum coagulation regime should theoretically provide the best results, practical considerations limit its performance. It is possible to obtain Norit membranes that have an internal diameter of 1.2mm, although floc sizes are still likely be a problem. A potential solution to this problem could be to change the membrane design from tube-side feed hollow fibres to a submersed membrane module with a shell-side feed, which would eliminate the problem of floc growth.

7.3.3 Zenon membrane experiments

To show the effect coagulation pre-treatment has on membrane performance, experiments were conducted with the optimised regime of 4 minutes slow mixing and with a reduced mixing time of 2 minutes. At 2 minutes slow mix, there is still excess iron in solution (see **Chapter 6, Fig 6.18**) and at 4 minutes this excess iron is reduced. The membrane was run for ten minutes before 2 minutes of back flushing was conducted with permeate (**Fig 7.12**)

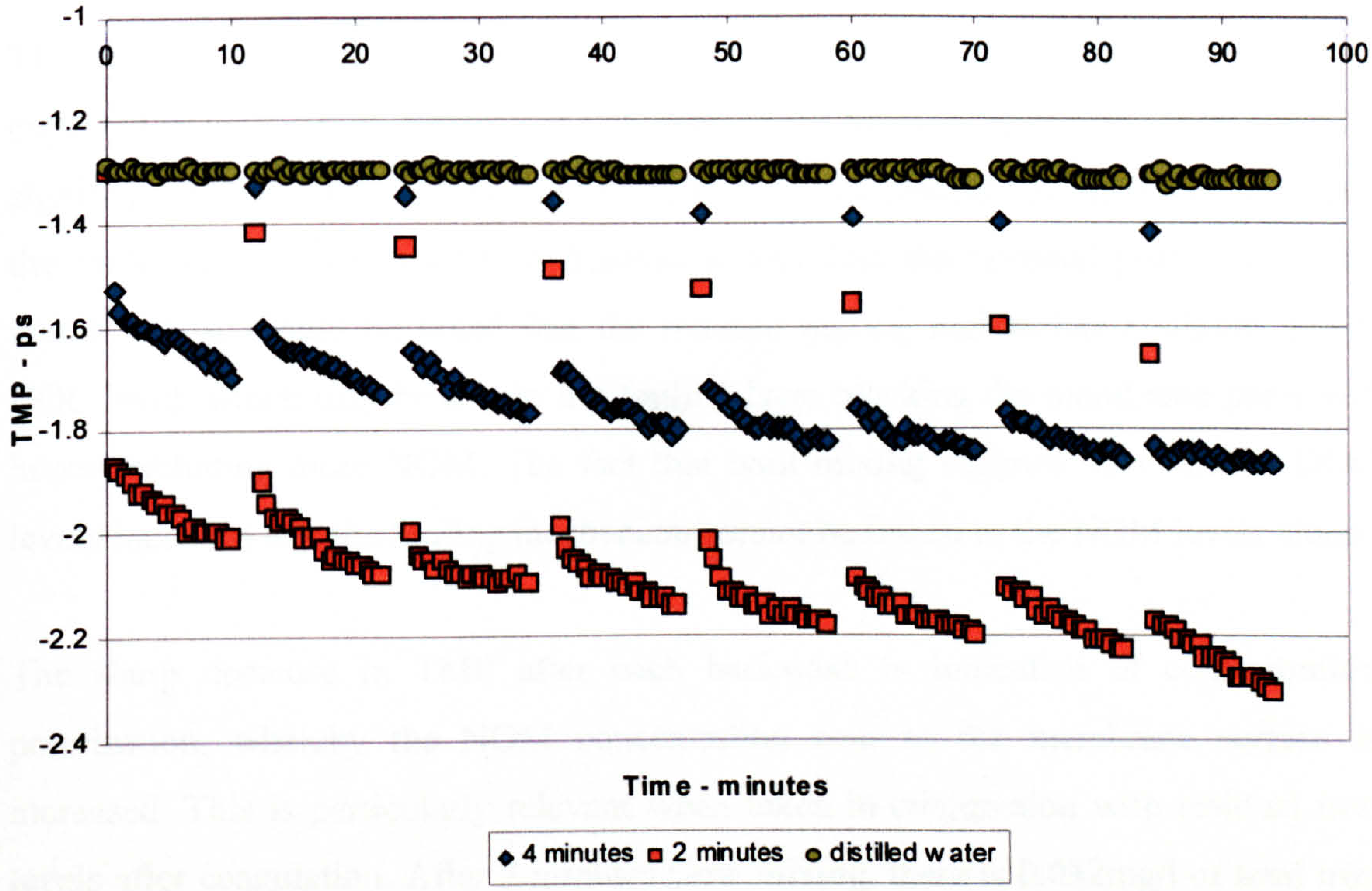


Fig 7.12 membrane performance with different slow mixing coagulation regimes

The results show that the performance of the membrane improved with 4 minutes of slow mixing; however, both coagulation regimes show significant levels of progressive fouling. Although the backwash initially recovers the performance, indicating some reversible fouling, the rapid and steady decrease over repeated cycles indicates that irreversible fouling is the main cause of poor membrane performance.

As shown in **Chapter 6**, the majority of NOM is removed by coagulation after rapid mixing and the main difference in the slow mixing regimes is the resulting level of residual iron. Table **7.1** shows the NOM analysis of the permeate of the different mixing regimes at the end of the last backwash cycle.

DOC parameters	Raw Water (mg/l)	2 minutes mixing (mg/l)	4 minutes mixing (mg/l)
Fulvic acids	3.8	0.5	0.6
Humic acids	1.3	0	0
Hydrophilic acids	1.2	0.4	0.4
Hydrophilic neutrals	2.1	1.8	1.9
Total	8.4	2.7	2.9

Table 7.1 DOC analysis of raw water and membrane permeate

The results show that the levels of fulvic and humic acids are reduced, which is expected as coagulation removes the charged NOM fraction. However, There is still a significant percentage of LMW acids and hydrophilic neutrals in the permeate, since the molecular size of this NOM fraction is less than the nominal pore size of the membrane. It should be noted that the reduced mixing regime has a slightly lower DOC level, which may be due to the fouling layer blocking the membrane pores and hence excluding more NOM. The fact that both mixing regimes have similar DOC levels indicates that the fouling mechanism cannot be linked to the NOM levels alone.

The sharp decrease in TMP after each backwash is indicative of concentration polarization, whereby the NOM concentration near to the membrane surface is increased. This is particularly relevant when taken in conjunction with residual iron levels after coagulation. After 2 minutes slow mixing, there is 0.032mg/l of total iron compared to 0.018mg/l with 4 minutes of slow mixing. Research has shown that metal ions, which remain in solution, can form complexes with the NOM in the feed solution. During filtration, the increase in NOM concentration near the membrane surface due to concentration polarization increases the complex formation. The complexes adsorb onto the membrane surface, giving rise to a decreased flux and also an increase in retention of the NOM complexes (Maartens A. et al., 1998).

When the membrane permeate was analysed for total iron the 2 minute mixing regime had 0.022mg/l compared to 0.013mg/l for the 4 minute mixing regime. As the 2 minutes slow mixing had 0.032mg/l of residual total iron after coagulation compared to 0.018mg/l with 4 minutes of slow mixing, this indicates that the membrane with the reduced mixing time removed twice the amount of iron. When taken in conjunction with the reduced DOC level in the permeate of the 2 minute mixing regime, the results indicate that the fouling mechanism is due to iron – NOM complexes being adsorbed onto the membrane surface.

The rapid decrease in permeate pressure after each backwash is due to the backwash only disturbing the concentration polarization layer, which on resumption of normal flow quickly reforms at the membrane surface. This is more pronounced at the lower mixing regimes, where there are a greater numbers of small flocs. As mixing time increases, the number of flocs decreases and their size increases, allowing them to settle. **Fig 7.13** shows the improvement in membrane performance when the coagulation mixing regime is extended to 8 minutes.

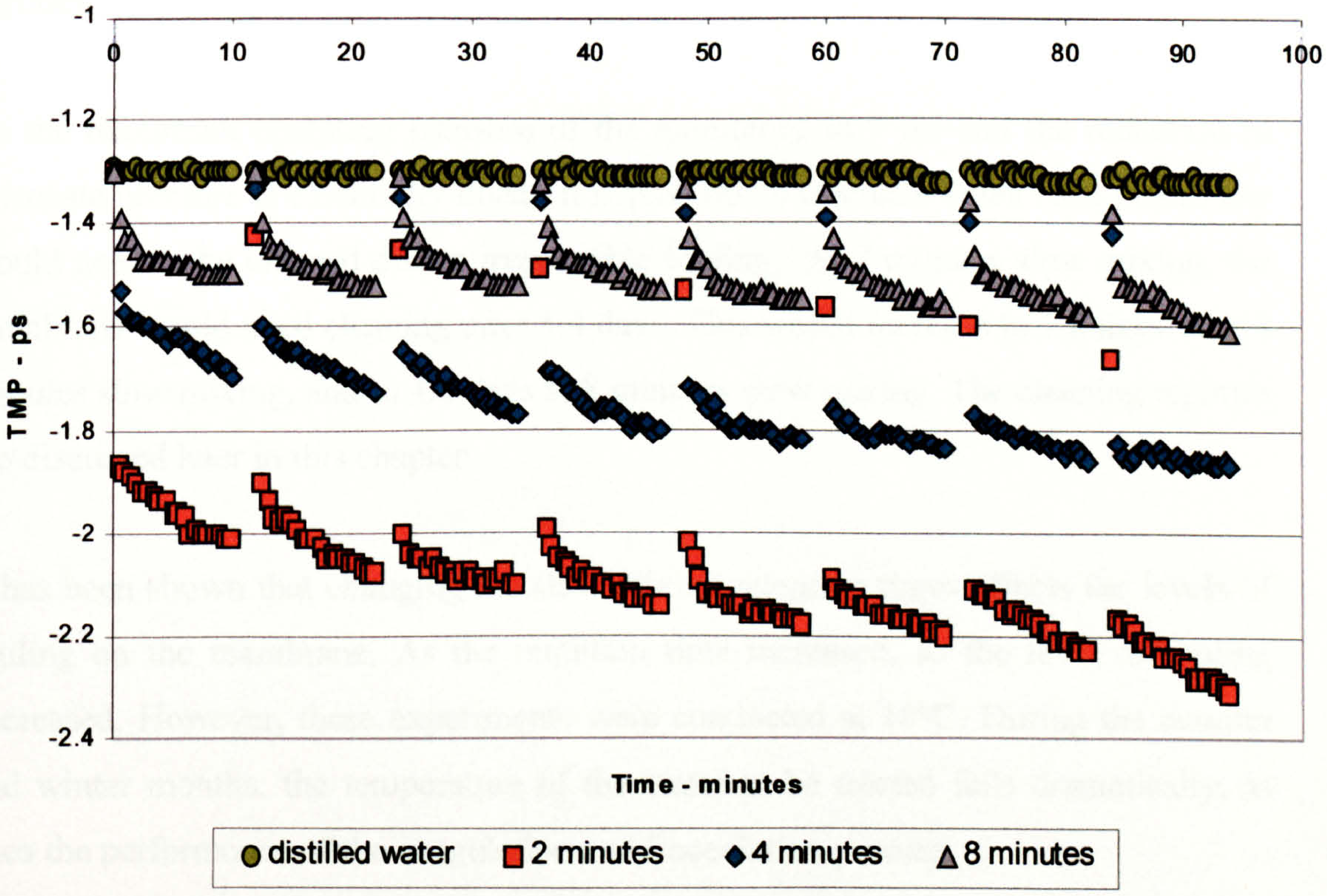


Fig 7.13 Membrane performance with extended coagulation mixing times

Fig 7.13shows the differences in permeate pressure between 2, 4 and 8 minutes of slow mixing. The increase in slow mixing time allows the flocs to grow larger and consequently, impurities in the water are enmeshed, which reduces the DOC level in the membrane permeate (**Table 7.2**). By decreasing the NOM and residual iron levels, and by increasing the mixing time, the concentration polarization effect is reduced and as a result reduces the fouling levels.

DOC parameters	Raw Water (mg/l)	2 minutes mixing (mg/l)	4 minutes mixing (mg/l)	8 minutes mixing (mg/l)
Fulvic acids	3.8	0.5	0.6	0.2
Humic acids	1.3	0	0	0
Hydrophilic acids	1.2	0.4	0.4	0.3
Hydrophilic neutrals	2.1	1.8	1.9	1.5
Total	8.4	2.7	2.9	2.0

Table 7.2 DOC analysis of membrane permeate with increased coagulation mixing regimes

As the maximum operating pressure of the membrane is 9 psi and the reduction in permeate pressure is essentially linear, it is possible to calculate when each membrane would need to be cleaned due to irreversible fouling. At 2 minutes slow mixing, the membrane would need cleaning after 1.4 days. This would increase to 1.8 days with 4 minutes slow mixing, and to 4.8 days at 8 minutes slow mixing. The cleaning regimes are discussed later in this chapter.

It has been shown that changing the slow mixing retention times affects the levels of fouling on the membrane. As the retention time increased, so the level of fouling decreased. However, these experiments were conducted at 18°C. During the autumn and winter months, the temperature of the water to be treated falls dramatically, as does the performance of the coagulation and flocculation process.

7.3.4 Incomplete coagulation

As discussed in **Chapter 6.3.6** (The temperature effect), there is a significant decrease in performance as temperature decreases. At 20.0°C, the excess iron is removed by enmeshment after 4 minutes. As temperature falls, the time required to remove the iron increases. At 4.2°C, ferric sulphate still remains that have not coagulated to form flocs after rapid mixing and even after 14 minutes there is still significant iron left in solution. These results, taken in conjunction with the interaction between NOM and metal ions in the concentration polarization zone, would indicate significant fouling of the membrane during cold temperature periods. This problem will be exacerbated by overdosing of the coagulant.

It has been shown that organically bound iron fouls the membrane; however, it should be determined if it is the sole fouling mechanism or if fouling is a combination of factors. Experiments were conducted to investigate this. A coagulant dose of 0.3mg/l Fe^{3+} was added to distilled water and filtered through the membrane to determine the effect over dosing has on the membrane **(Fig 7.14)**.

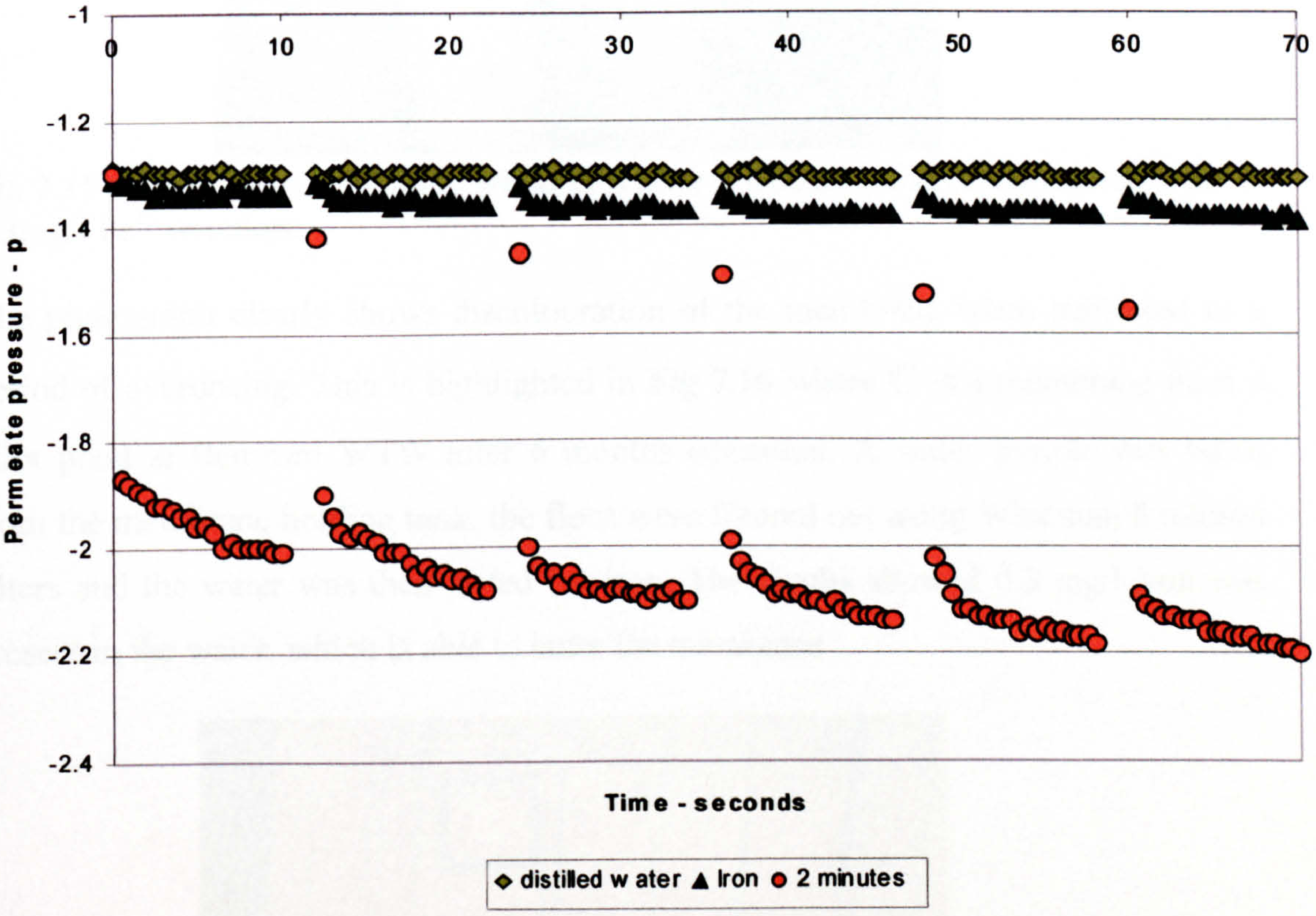


Fig 7.14 The effect of iron on membrane performance compared to normal operation with 2 minutes of slow mixing

The results show that excess iron in solution deteriorates the performance of the membrane. The deterioration is slight when compared to the reduction in the case of the coagulated raw water, as there is no NOM to interact with. Both types of fouling are irreversible, and require chemical cleaning. The impact of iron fouling the membrane is however a long term problem.

Fig 7.15 shows two Zenon ZW-10 membrane modules, **A** is a clean membrane, while **B** is a membrane after 2 weeks operation conducted with a 0.3mg/l Fe^{3+} coagulant overdose.

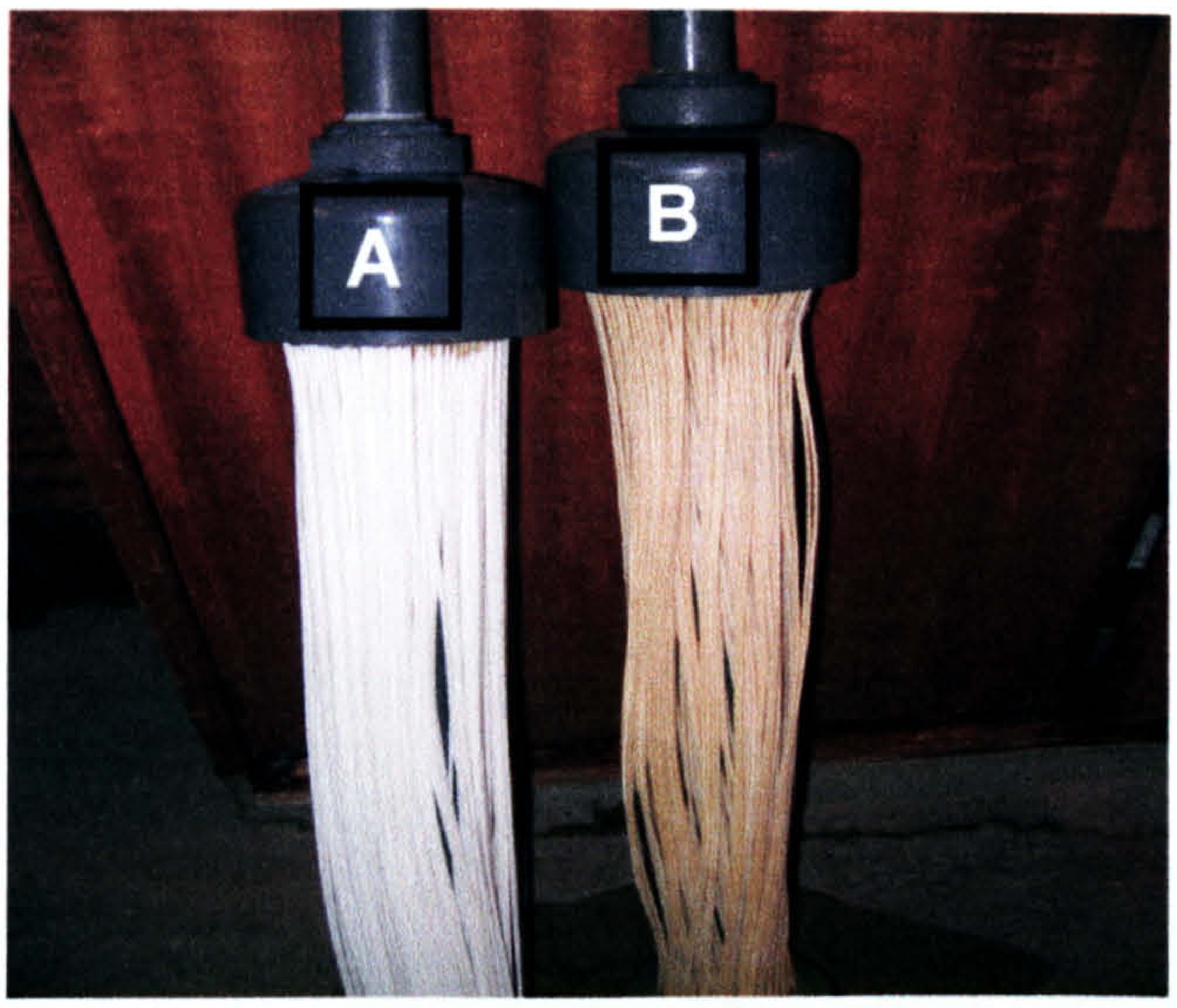


Fig 7.15 **A** is a clean membrane, while **B** is after 2 weeks operation conducted with 0.3mg/l Fe^{3+} overdose.

The photograph clearly shows discolouration of the membrane when subjected to a period of overdosing. This is highlighted in **Fig 7.16** where **C** is a membrane from a pilot plant at Bamford WTW after 6 months operation. A water sample was taken from the membrane holding tank, the flocs were filtered out using Whatman 8 micron filters and the water was then tested for iron. The results showed 0.3 mg/l iron was present in the water, which is able to enter the membrane

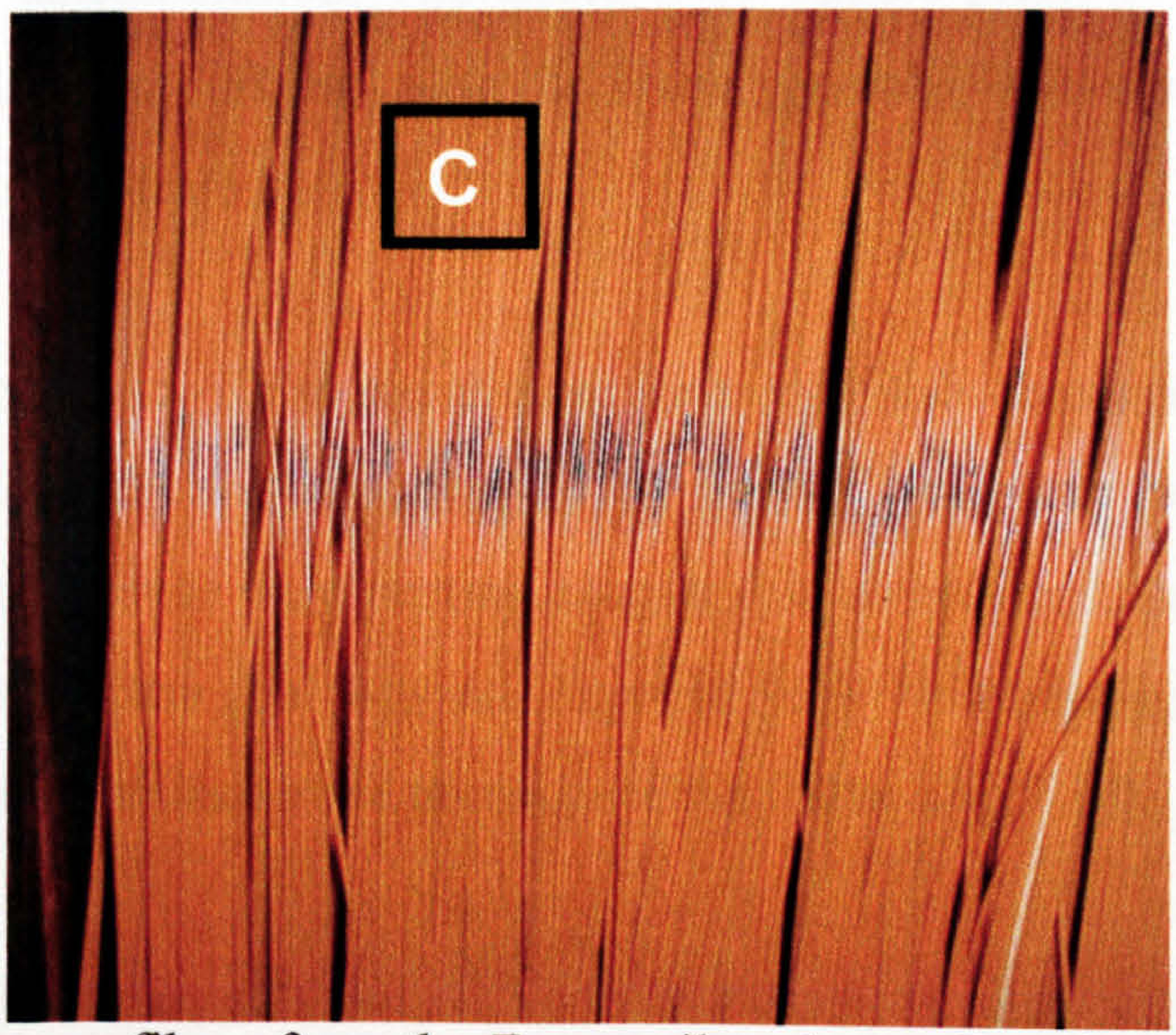


Fig 7.16 membrane fibres from the Zenon pilot plant at Bamford WTW

SEM analysis was conducted on a fibre from membrane **C** and shows the surface is covered with a deposit (**Fig 7.17**).

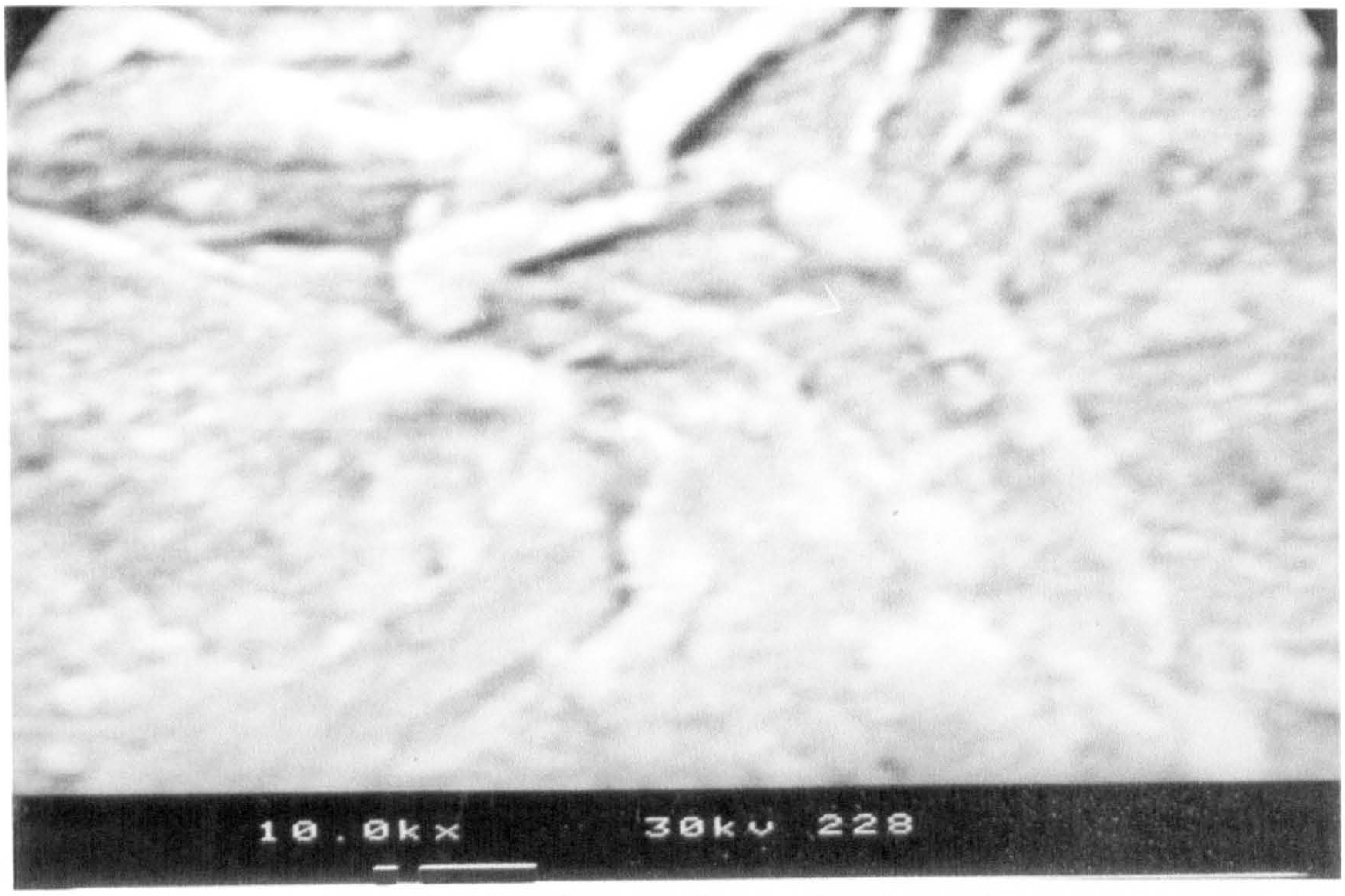


Fig 7.17 SEM analysis of ultrafiltration membrane after 6 months use

A section of the fouled membrane was placed in distilled water and heated to 80°C. This dissolved the foulant into solution. Spectrophotometer analysis confirmed the presence of iron in solution.

Although the membrane had been subjected to regular cleaning cycles, it had little impact on the discolouration. The fibres were stained pretty evenly, with the colour ranging from light to dark tan, with the fibres generally lighter at the ends and darker in the middle of the fibre.

The integrity of some of the membrane fibres was also damaged. Many of the fibres had a rough texture, and shedding of the active layer was occurring, where little pieces of the membrane were peeling away and in some cases, the braid could be seen through the membrane (but was not exposed yet). This phenomenon was especially severe on the badly discoloured portions of the fibres (**Fig 7.18**).

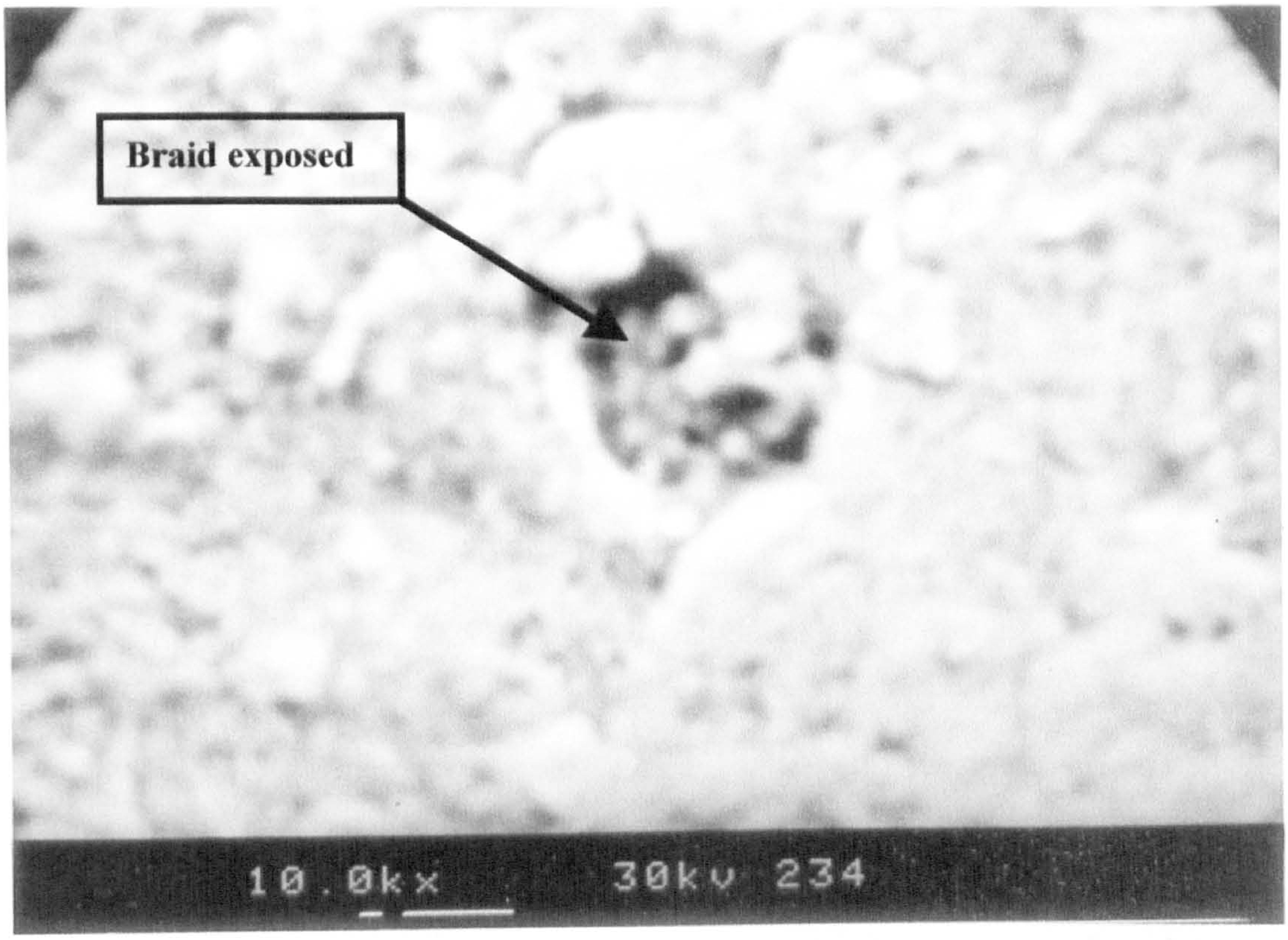


Fig 7.18 SEM of Zenon membrane showing integrity of membrane damaged due to fouling

With the correct coagulant dose and mixing regime, the fouling of the membrane is due to NOM and can be remedied by normal chemical cleaning (hydrochloric acid and sodium hypochlorite). This, however, does not remove the iron left on the membrane by overdosing. Analysis was conducted on various cleaning regimes to determine the best possible method of recovering the membrane.

7.3.5 Zenon membrane cleaning study

To investigate the cleaning regime, the raw water treated with 3 mg/l $^{Fe3+}$ coagulant was run through the membrane was run with periodic backwash until the TMP reached -9 psi. Experiments were conducted firstly with the optimum coagulation regime and secondly with the same regime but with 0.5mg/l $^{Fe3+}$ excess coagulant. Once the membrane had been fouled, the module was then soaked in a cleaning solution for 4 hours before rinsing. The cleaning solutions investigated were sodium hypochlorite, hydrochloric acid, EDTA and sodium bisulphate. The tests were run at various temperatures (4°C, 18°C and 35°C). Distilled water was then run through the membrane to measure a recovery rate. **Fig. 7.19** shows percentage recovery rates, after cleaning of the membrane used to treat water with the optimum coagulation regime, at the three different temperatures. All chemical solutions were 1000ppm per litre.

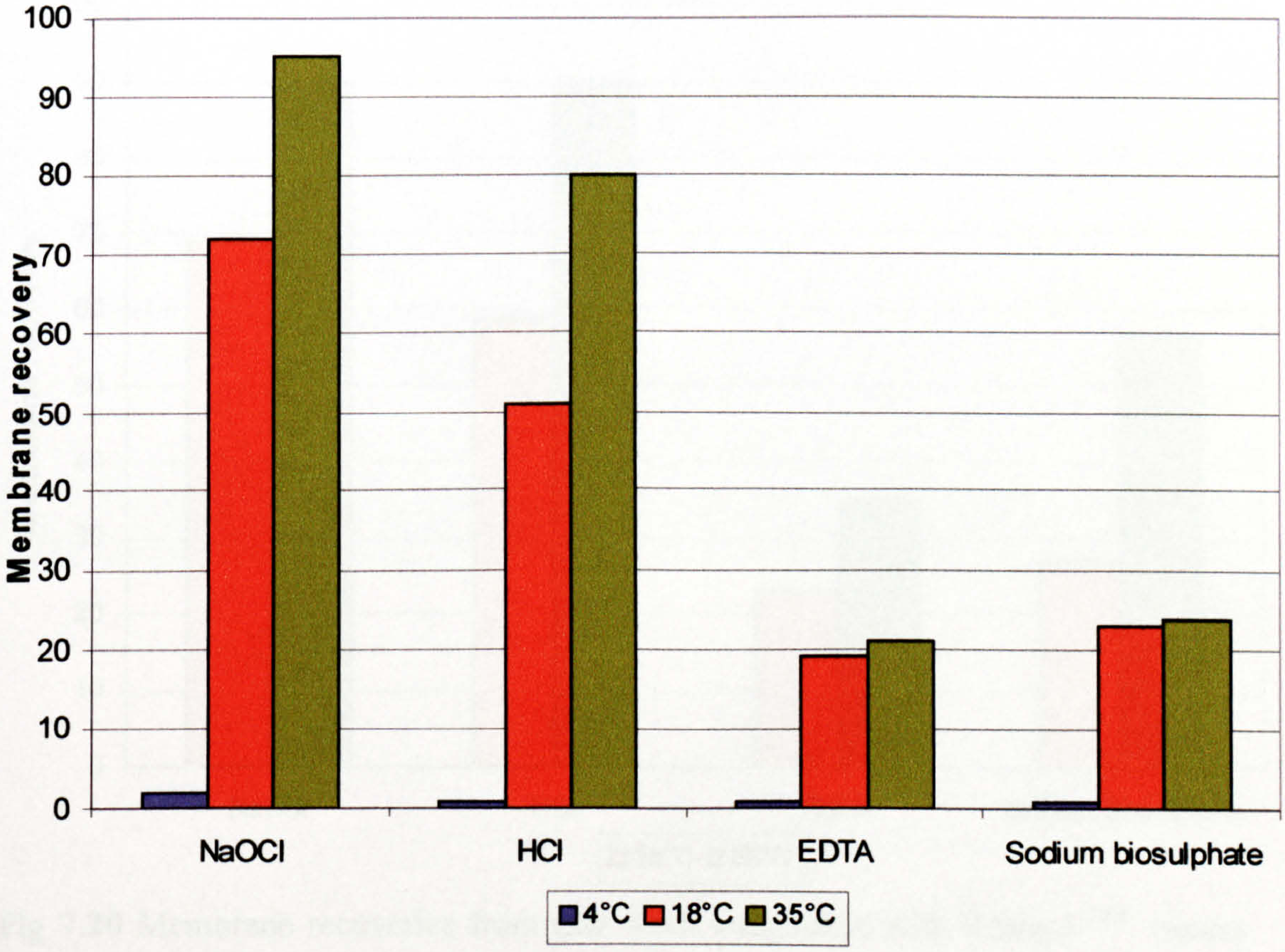


Fig 7.19 Membrane recovery for optimised coagulation regime with chemical cleaning at three different temperatures

The results show that there is little or no improvement with any of the chemicals when the membrane is cleaned at 4°C. This indicates that, for the cleaning solutions to react with the fouling layer, elevated temperatures are required.

At normal summer operation temperatures, the recovery of the membrane is best when cleaned with sodium hypochlorite (72%), indicating the presence of organic based foulants. This rises to 95% when elevated temperatures are used. The positive recovery of the membrane performance with hydrochloric acid, EDTA and sodium bisulphate indicate the presence of some inorganic material. The effectiveness of hydrochloric acid increased considerably at elevated temperatures.

Since there was no improvement at 4°C, the tests were conducted with the membrane fouled when raw water was coagulated with 0.5mg/l $^{Fe3+}$ excess coagulant, at 18°C and 35°C **(Fig 7.20)**

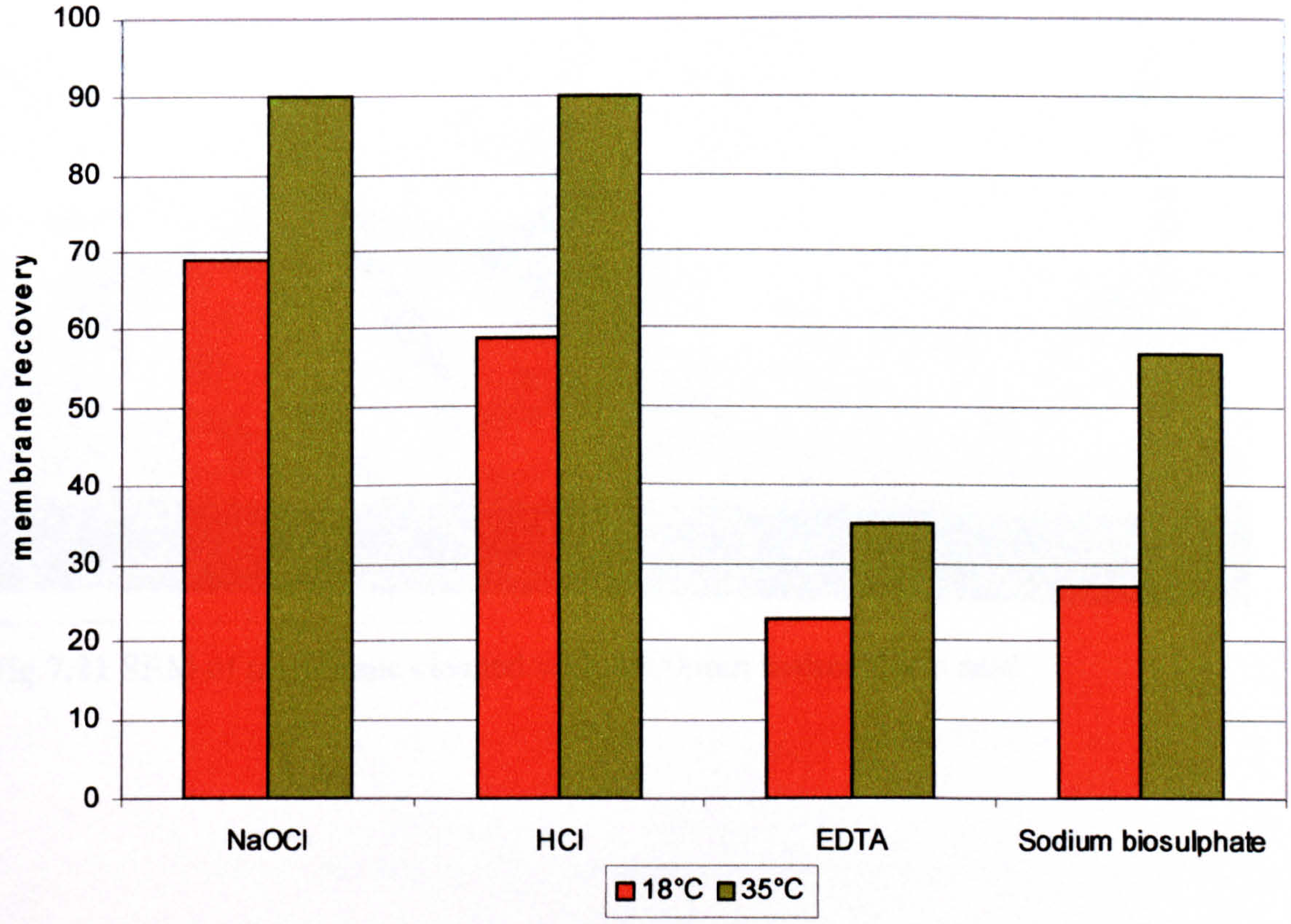


Fig 7.20 Membrane recoveries from raw water coagulated with 0.5mg/l $^{Fe3+}$ excess coagulant, with chemical cleaning at two different temperatures

The results follow a similar pattern, with sodium hypochlorite performing better at 35°C. However, the recovery rates of hydrochloric acid, EDTA and sodium bisulphate are all increased, indicating an increase in fouling by inorganic material. Again, hydrochloric acid was more effective at elevated temperatures. The sodium bisulphate showed some improvement but was not as efficient at HCl.

Although none of the cleaning regimes alone recovered the membrane performance 100%, the possibility of raising the cleaning chemical concentration (**Fig 7.21**) or further increasing the cleaning temperature (**Fig 7.22**) to improve recovery could in fact damage the membrane permanently.

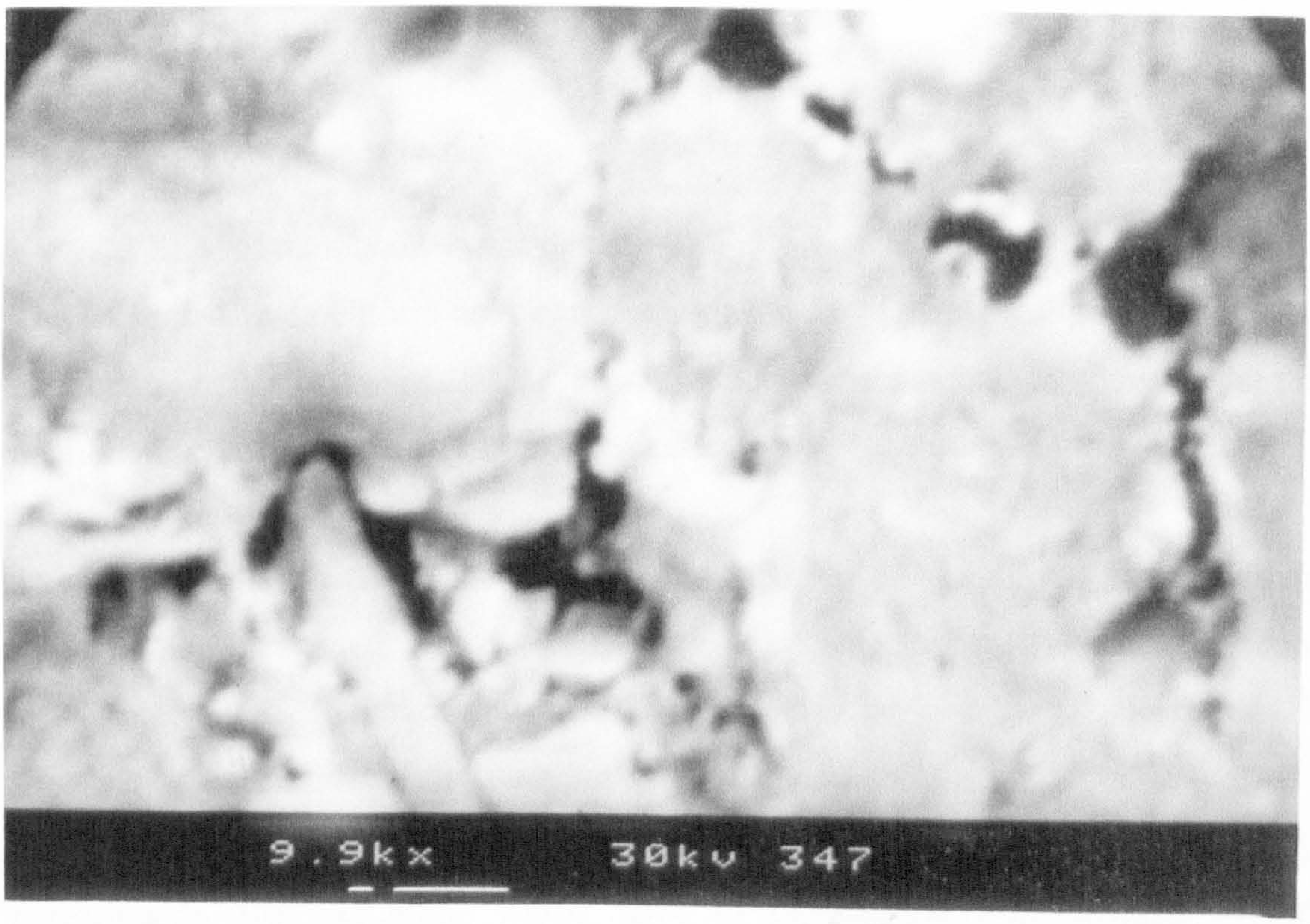


Fig 7.21 SEM of membrane cleaned with 4000ppm hydrochloric acid

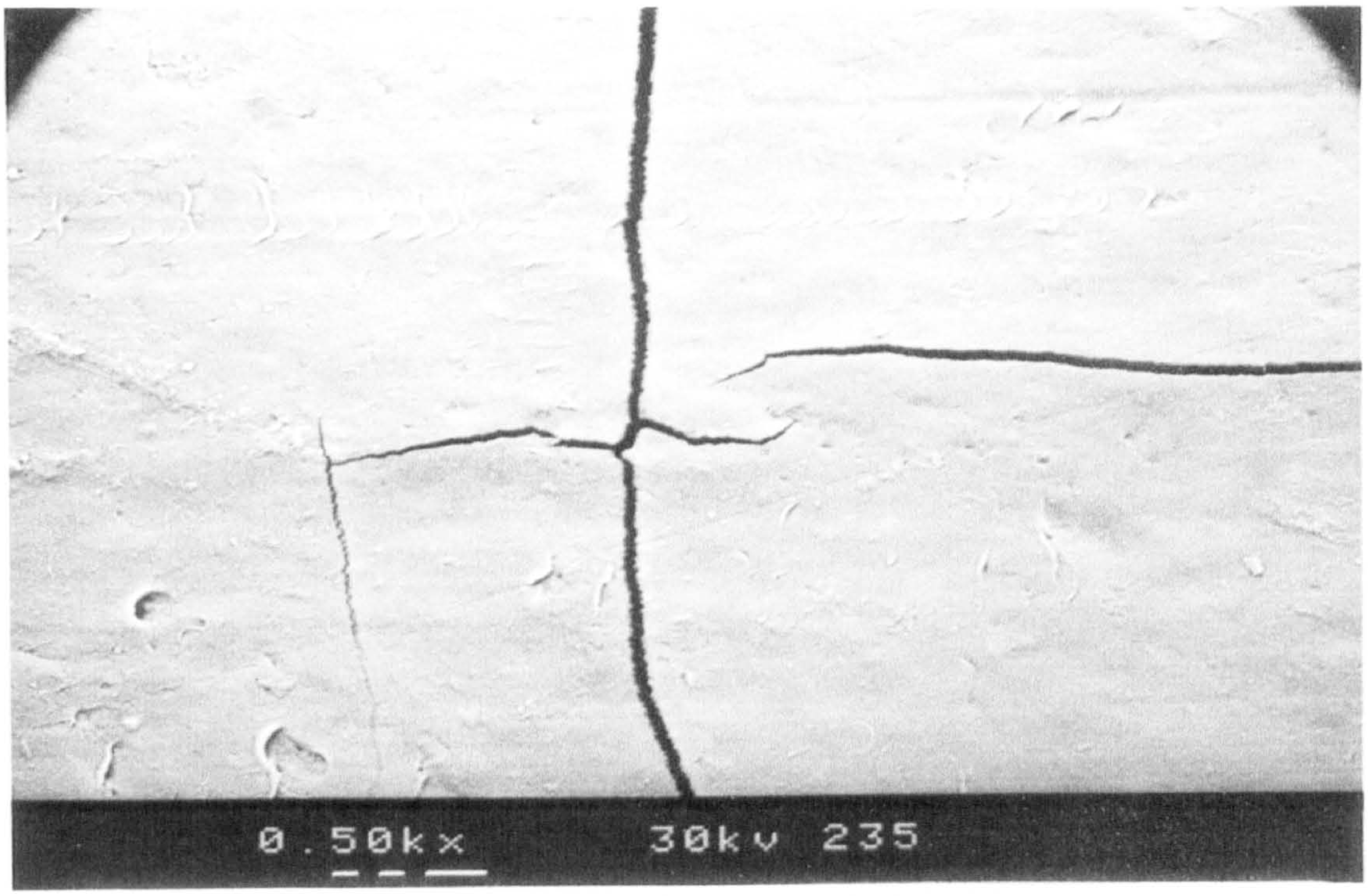


Fig 7.22 SEM of membrane cleaned at 50°C

The increased hydrochloric acid concentration destroys the membrane, leaving the membrane braids exposed, while cleaning the membrane at 50°C expands the membrane, cracking the active ultrafiltration membrane layer.

The results mimic closely an analysis conducted by the membrane manufacturers Zenon. They conducted a study on fibres taken from the heavily fouled Bamford WTW membrane. They recommended that, to recover the membrane performance, it first had to be cleaned with 1000ppm sodium hypochlorite at 35°C, followed by a 2000ppm hydrochloric acid solution. They also recommended that to maintain the performance, the membrane would have to be cleaned with 500ppm sodium hypochlorite at 35°C to remove the organic foulants, rotated every third cleaning cycle with 2000ppm hydrochloric acid, to remove any inorganic foulants.

The results from the cleaning study, taken in conjunction with the membrane filtration experiments show that the fouling of the membrane is due to a combination of organic material and iron. The fouling is exacerbated if an incorrect coagulation dose is applied.

As all the experiments were conducted using upland source water from Bamford WTW, experiments were also conducted with raw water from Draycote WTW to determine if the fouling mechanisms would remain constant with a lowland water source.

7.3.6 Lowland water experiments

Experiments were conducted with the ZW-10 test rig to determine firstly if stand-alone UF was capable of treating the Draycote water. **Fig 7.23** shows the changes in permeate pressure during the experiments with no coagulation as well as the permeate TOC levels.

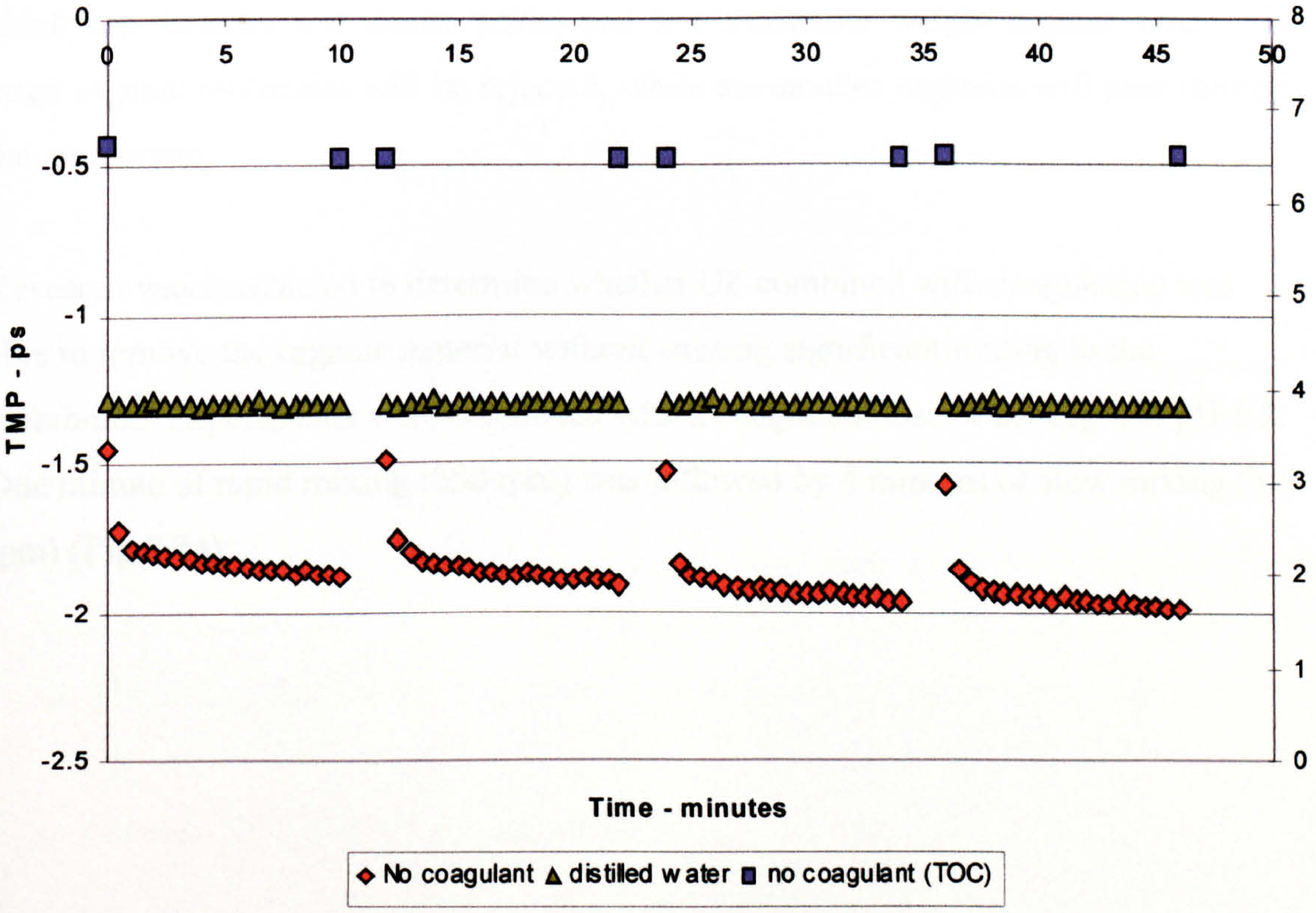


Fig 7.23 Changes in TMP of Draycote water with no coagulant including permeate TOC levels

The ultrafiltration of Draycote water without coagulation shows fouling problems as indicated by the sharp fall in permeate pressure. By taking the maximum operating pressure as 9 psi, it is calculated that chemical cleaning would be required after only

1.2 days. With regards to TOC levels, the raw water level of 8.5 mg/l falls to 6.5 mg/l in the permeate. This indicates that UF alone is not sufficient to treat this type of water. The answer to why UF alone does not significantly reduce TOC levels is due to the relationship between the membrane nominal pore size and the size of the particles to be rejected.

The ZW-10 has a pore size of 0.04μm and, although it will reject large organic molecules without coagulation, organic material smaller than 0.04nm will pass through the membrane. As shown in Chapter 4, Draycote water is composed of Polysaccharides (including amino sugars, polypeptides and proteins); Humics (molecular weight ~1000 g/mol.); Building Blocks (humic hydrolysates with molecular weight between 300 – 450 g/mol.); Neutral Amphiphilics (alcohols, aldehydes, ketones and amino acids) and low molecular weight organic acids. The large organic molecules will be rejected, while the smaller organics will pass through the membrane.

Research was conducted to determine whether UF combined with coagulation was able to remove the organic material without causing significant fouling to the membrane. Experiments were conducted with a coagulant dose of 2.4 mg/l, at pH 5.3. One minute of rapid mixing (250 rpm) was followed by 4 minutes of slow mixing (30 rpm) (Fig 7.24).

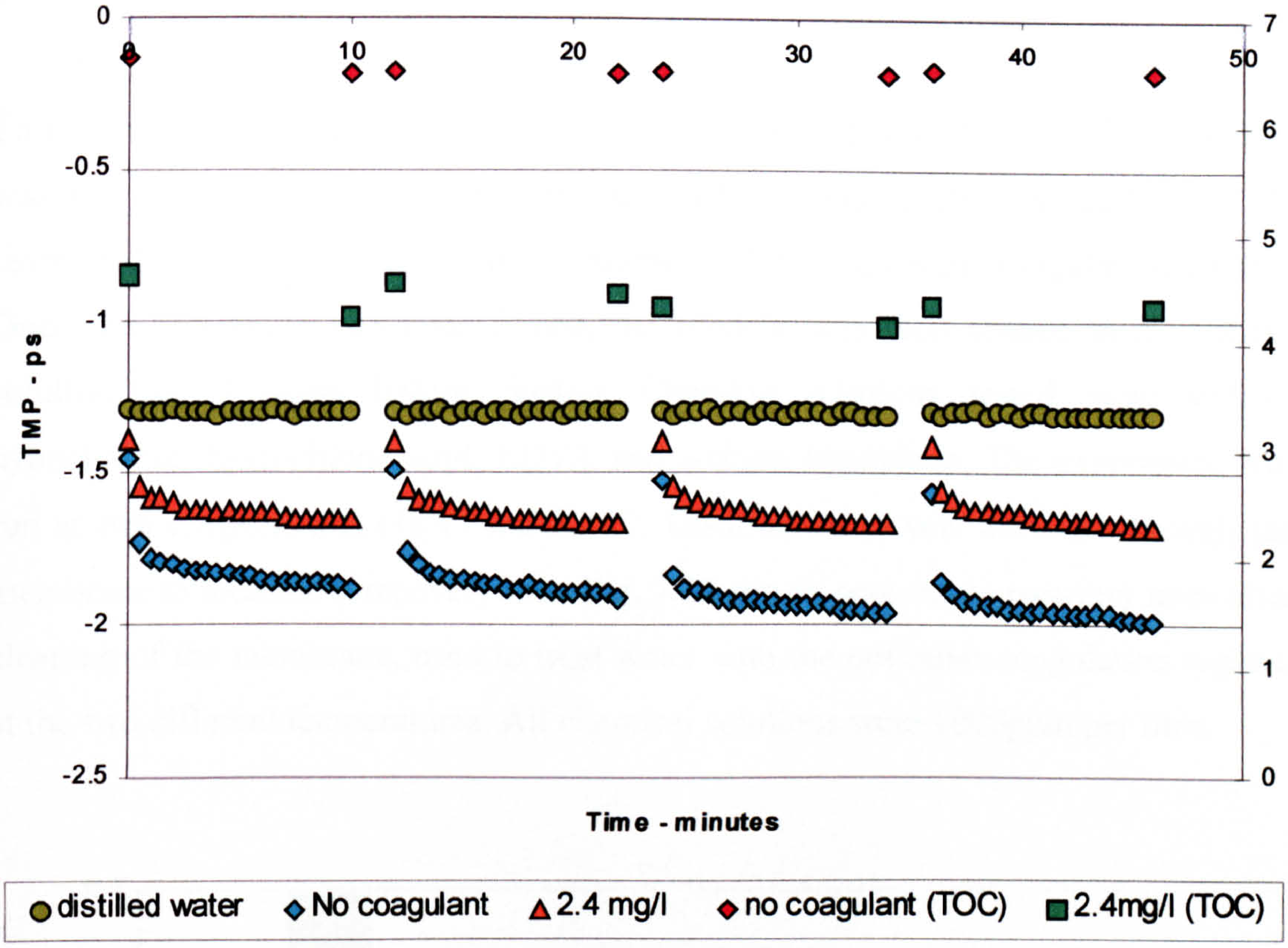


Fig 7.24 Membrane performance with and without coagulant, including permeate TOC analysis

The use of coagulation improves the membrane performance significantly after only 4 minutes of slow mixing. However, the permeate TOC levels were only reduced from 8.5mg/l to 4.5 mg/l, leaving over 47% of the organics in the permeate. Coagulation will only remove the charged humics, while the size exclusion of the ultrafiltration membrane will only reject the polysaccharides.

By increasing the length of slow mixing, enmeshment of the water impurities by the growing flocs will increase, but not sufficiently to reduce the permeate TOC levels by more than a few percent. Increasing the coagulant dose will also not improve the membrane performance, as it cannot remove particles that are not charged, In fact an increase in coagulant dose will lead to the same problems as experienced while treating Bamford water. The excess iron will increase the fouling levels and require the membrane to be cleaned more frequently.

7.3.7 Lowland water cleaning experiments

To investigate the cleaning regime, the raw water treated with 2.4 mg/l $^{Fe3+}$ coagulant was run through the membrane was run with periodic backwash until the TMP reached -9 psi. Experiments were conducted with the optimum coagulation regime. Once the membrane had been fouled, the module was then soaked in a cleaning solution for 4 hours before rinsing. Cleaning solutions tested were sodium hypochlorite, hydrochloric acid, EDTA and sodium bisulphate. The experiment was run at two temperatures (18°C and 35°C). Distilled water was then run through the membrane to measure a recovery rate. **Fig. 7.25** shows percentage recovery rates after cleaning of the membrane, used to treat water with the optimum coagulation regime, at the two different temperatures. All chemical solutions were 1000ppm per litre.

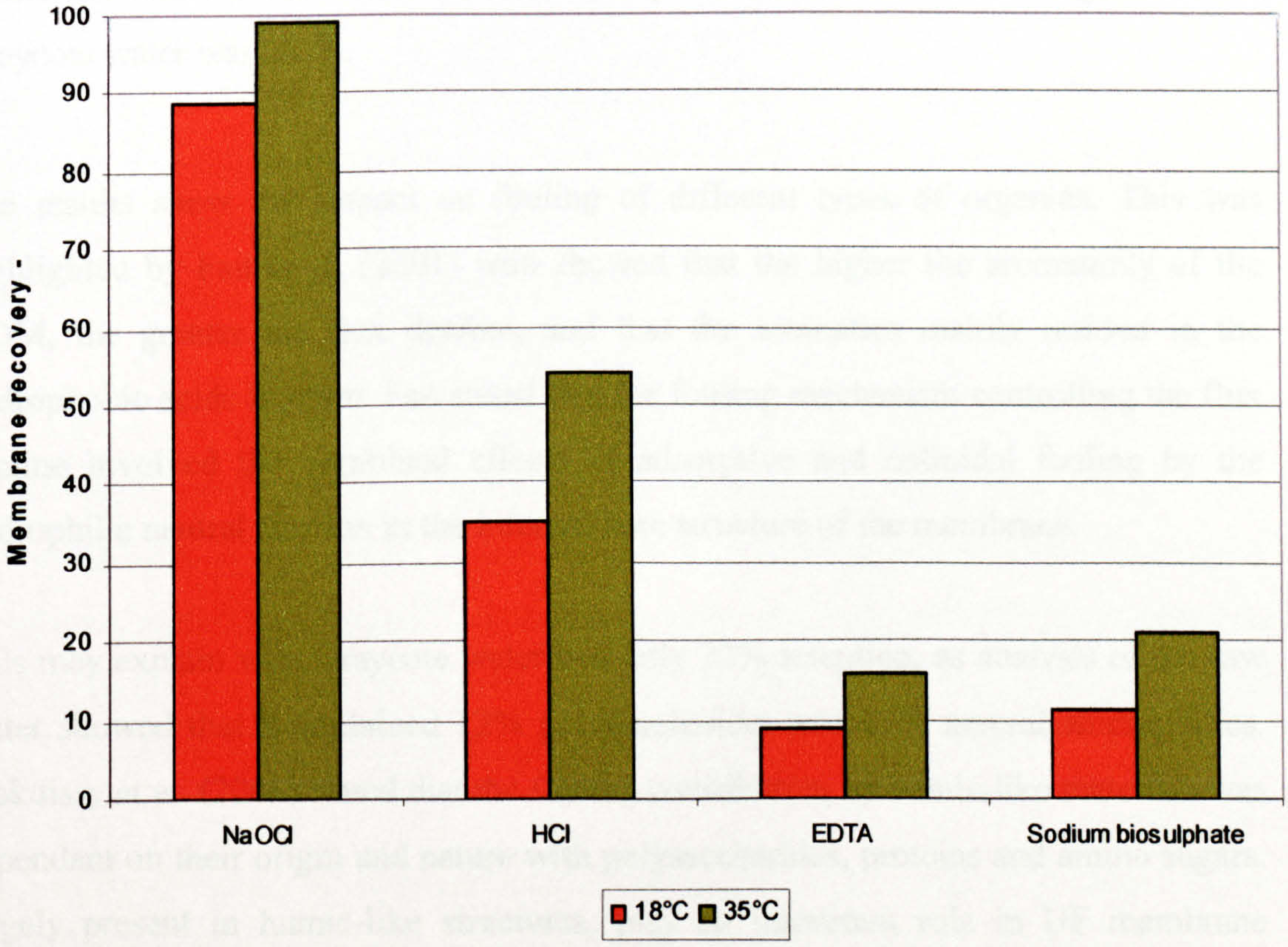


Fig 7.25 Membrane recovery from optimised coagulation regime (Draycote water) with chemical cleaning at two different temperatures

At normal summer operation temperatures, the recovery of the membrane is best when cleaned with sodium hypochlorite (89%), indicating the presence of organic based foulants. This rises to 99% when elevated temperatures are used. Compared to the results from the cleaning study of Bamford water, the effectiveness of hydrochloric acid, EDTA and sodium bisulphate is much reduced, even at elevated temperatures. This indicates that the main fouling mechanism when treating Draycote water is due to NOM. This may be in the form of surface adsorption or pore blocking, but techniques available during this research limit this to speculation.

7.4 Conclusions

To assess the performance of coagulation upfront of the ultrafiltration membranes, experiments were first conducted without the coagulation stage. For the experiments conducted on Bamford water, the retention of organics for both the Norit and Zenon membrane was ~40 %. While the retention by the Zenon membrane of organics from Draycote water was 23 %.

The results show the impact on fouling of different types of organics. This was highlighted by Fan et al. (2001) who showed that the higher the aromaticity of the NOM, the greater the flux decline, and that the aromatics mainly resided in the hydrophobic acids fraction. Fan stated that the fouling mechanism controlling the flux decline involved the combined effects of adsorptive and colloidal fouling by the hydrophilic neutral fraction in the internal pore structure of the membrane.

This may explain why Draycote water had only 23% retention, as analysis of the raw water showed that it contained 12% polysaccharides and 17% neutral amphiphilics. Makdissy et al. (2004) stated that the fouling contribution by humic-like materials was dependant on their origin and nature with polysaccharides, proteins and amino sugars, largely present in humic-like structures, play an important role in UF membrane fouling.

To improve the performance of the membranes, an optimised coagulation regime was implemented. The use of the optimised regime on the Norit membrane resulted in the large flocs formed by the optimum coagulant regime blocking the hollow fibre tube (internal diameter 0.8mm), resulting in a steady reduction of permeate flow. This phenomenon has been reported by Lerch, A., S. Panglisch, et al. (2004) who stated that this is due to the particle being larger than the so called 'cork forming diameter' causing clogging of the capillary, leading to a gradual increasing of the developed plug, i.e. a decrease of the usable membrane surface, by further deposited particles.

To resolve this issue a revised coagulation regime was implemented where the slow mixing time was reduced. Although this has the benefit of reducing the floc size, it increases the amount of residual iron in solution.

The results showed that the TOC content of the permeate was 0.1mg/l with ferric sulphate. This is significant, as coagulation reduces the TOC to 0.3 mg/l (**Chapter 6, Fig. 6.16**). This indicates that a fraction of the organic neutrals, that is not removed by coagulation. is removed by the combined coagulation/membrane filtration process. Indicating that adsorption of the un-coagulated fraction onto the membrane is taking place. However it should be noted that the improvement in permeate quality is 90%. This is an increase of 67% over ultrafiltration of the raw water.

The use of the Zenon membrane on the other had produces a different result. Theoretically, as both membranes have the same nominal pore size and are both hydrophilic, the results should be similar. However the permeate quality of the Zenon membrane with the optimised coagulation regime was only 66%. This increased to 76% when the coagulation slow mixing regime was increased to 8 minutes (See **Table 7.2**) due to enmeshment of neutral organics in larger flocs.

The result show that, although the levels of fulvic and humic acids are reduced, which is expected as coagulation will remove the charged NOM fraction, there was still a significant percentage of hydrophilic neutrals in the permeate.

The fact that the Norit, with the same nominal pore size, produced better results may be due to a combination of factors. Firstly, the experiments with the Zenon were conducted during the summer periods, while the Norit experiments were conducted during the autumn and winter. Although no fractionation analysis was carried out on the Norit permeate it can be theorised that the differences were due to the time of year and seasonal variations in NOM type. Scott et al., (2001) stated that during a four-year study, they observed variations in the hydrophilic content of the water ranging between 20 and 80%, with the dissolved organic matter increasing in hydrophilicity during the summer months. They hypothesized that the observed variations throughout the year could be explained in relation to microbial driven mechanisms of DOC release. As already stated Bamford water was susceptible to algal blooms during the summer.

The differences in permeate quality between the two membranes could also be explained by formation of a cake on the Norit membrane surface. When operated at a higher pressure a compacted cake formed on the membrane surface. Guigui C. et al., (2002) conducted experiments that showed the formation of a floc cake could retain even the smallest particles. This may explain why the permeate quality of the Norit was better, as the compressed cake on the membrane surface acted as a secondary filter trapping the type of organics that passed through the Zenon, who's submerged nature limits the formation of a dense floc cake.

Conventional thinking indicates that a compressed cake leads to more severe fouling levels which is not removed by backwashing (Decarolis J. et al., 2001).. Although a compressed cake was formed when the Norit was run with a higher pressure, the Norit membrane design with the backwashing regime was able to remove the majority of compressed cake layer, although over numerous cycles the backwash efficiency was reduced. Bessiere Y. et al., 2005 also showed that a higher operating pressure lead to an increase in fouling, with reduced backwashing efficiency

Although the Norit membrane had a better permeate quality that the Zenon membrane, 90% removal of DOC compared to 76%, there was a significant difference in performance in terms of type and level of fouling. Even by shortening the coagulation mixing time and operating at a higher pressure, the Norit membrane experienced severe fouling.

The level of reversible fouling was reduced by implementing a more frequent back wash regime (also shown by Kim et al (2005)). By increasing the frequency the fouling, due to capillary blocking with the optimum coagulation regime, was also reduced. However, the level of irreversible fouling was severe. It was calculated that the Norit membrane would require chemical cleaning after 1.1 days of continual use. The Zenon on the other hand had better performance, with the backwash regime able to remove the accumulate material and extend the membrane cycle to 4.8 days.

Even though both membranes showed good performance in terms of permeate quality when combined with coagulation, irreversible fouling still took place. This is a well-documented phenomenon. Kimura, K., et al. (2004) showed that although pre-coagulation/sedimentation significantly mitigated membrane fouling, mainly by the reduction of reversible type of membrane fouling, the degree of irreversible fouling was not reduced by the pre-treatment. This was because irreversible fouling caused by filtering the surface water examined in their study was mainly attributed to polysaccharides/protein like fractions of organic substances that cannot be efficiently removed by coagulation/sedimentation.

Also, Pikkarainen et al (2004) in their research stated that according to HPSEC UV254 data, neither clarification nor PC-MF were effective in removing low molecular weight UV254-absorbing organic materials. Their pilot scale tests indicated that coagulated raw water contained hydrophilic acid and hydrophilic non-acid fractions, which were partly adsorbed onto the membrane.

This inability of coagulation to remove different types of organics can also explain why the use of coagulation with the Zenon membrane to treat Draycote water only showed an improvement of 53% compared against 23% with ultrafiltration alone. Analysis of the water showed that the water only contained ~43% charged humic particles. As the removal efficiency was greater, this indicated that a percentage of the neutral organics also absorbed onto the surface causing irreversible fouling.

Although the preceding discussion was in relation to optimising the coagulation regime for NOM removal and showed that the coagulation regime had to be adapted to improve membrane performance, the consequence of this is excess iron remaining in solution. The aim of this thesis was to investigate the role of excess iron on the long term irreversible fouling of ultrafiltration membranes.

With regard to the Norit membrane, when the membrane permeate was analysed for total iron, the revised mixing regime (2 minutes) had 0.022mg/l compared to 0.013mg/l for the optimised mixing regime (4 minutes). As the 2 minutes slow mixing had 0.032mg/l of residual total iron after coagulation compared to 0.018mg/l with 4 minutes of slow mixing, this indicated that twice the amount of iron was removed by the membrane with the reduced mixing time. When taken in conjunction with the reduced DOC level in the permeate of the 2 minute mixing regime, the results indicate that the fouling mechanism is due to iron – NOM complexes being adsorbed onto the membrane surface.

As the level of excess iron can increase due to overdosing of the coagulant, and as shown in **Chapter 6.3.3**, a reduction in temperature also increases the residual levels of iron. The role of iron on long term membrane fouling was investigated further with the Zenon membrane. The results shown in **Fig 7.14**, where a coagulant dose of 0.3mg/l Fe^{3+} was added to distilled water and filtered through the membrane to determine the effect over dosing has on the membrane, indicated that excess iron in solution deteriorates the performance of the membrane.

This impact of iron is highlighted in **Fig 7.16** where a membrane from a pilot plant at Bamford WTW after 6 months operation is shown. A water sample was taken from the membrane holding tank, the flocs were filtered out using Whatman 8 micron filters and the water was then tested for iron. The results showed 0.3 mg/l iron was present in the water, which is able to enter the membrane.

The impact of iron on the long term fouling of the membrane was researched further with an investigation into the impact of various membrane cleaning regimes.

For the Norit membrane, after the optimum coagulation regime, the membrane recovers 96% of its original performance with a hydroxide clean. This compares favourably to the performance of hydrochloric acid (67%) and citric acid (74%) alone. With the revised coagulation regime, which has excess iron in solution, the results show that the sodium hydroxide cleaning performs less well. However, when the hydroxide soak is followed by a citric acid soak, the membrane recovers 100% of its performance. The results indicate that the fouling component for the revised coagulation regime is organically bound iron species, as opposed to fouling due to flocs blocking the membrane fibres with the optimum regime, as well as absorbed non-coagulated NOM.

The results for the chemical cleaning of the membrane when it is fouled by NOM are similar to that of research by Kumiura et al (2004). They showed that for their water an alkaline solution (NaOH) was more efficient than the chelating agent and the acid solutions in recovering membrane permeability. The oxidizing agent (NaClO) exhibited the best cleaning performance among the tested chemicals. Their results implied that some fractions of organic substances rather than inorganic ones caused the irreversible fouling

The investigation into the cleaning of the Zenon membrane show that with the correct coagulant dose and mixing regime, the fouling of the membrane is mainly due to NOM, and can be remedied by normal chemical cleaning (hydrochloric acid and sodium hypochlorite). However, this is where the problem of residual iron becomes apparent. As the fouling of the membrane by iron is minimal, it only becomes apparent after an extended period, as indicated by discolouration of the membrane fibres as shown in **Fig 7.16** after 6 months of use. At this point implementing a cleaning regime to recover the membrane may be problematic.

The deterioration, due to residual iron fouling, has been shown by Gabelich C. J. et al (2002), in their investigation of fouling in RO membranes. They showed that residual aluminium and iron, from alum and ferric chloride coagulation, degraded the membrane performance due to fouling. Although no solution to recover the membrane performance was given.

The investigation into the recovery of the Zenon membrane, fouled during coagulation with excess coagulant, showed that the temperature of the cleaning solution had a direct effect on the cleaning efficiency. At a temperature of 4°C, there was no improvement in flux recovery. At room temperature, the recovery by NaOCl was 68%, while HCl recovered the membrane performance by 59%; EDTA showed a 25% recovery, and Sodium bisulphate showed a 28% recovery. At an elevated temperature (35°C), NaOCl increased recovery to 90%. As the recovery rates of hydrochloric acid, EDTA and sodium bisulphate all increased as well, this indicated fouling by inorganic material.

However, none of the cleaning regimes alone recovered the membrane performance 100%, even at high temperatures. This research is in agreement with the membrane manufacturers who also investigated the cleaning of the fouled membrane. They recommended that, to recover the membrane performance, it first had to be cleaned with 1000ppm sodium hypochlorite at 35°C, followed by a 2000ppm hydrochloric acid solution. They also recommended that to maintain the performance, the membrane would have to be cleaned with 500ppm sodium hypochlorite at 35°C to remove the organic foulants, rotated every third cleaning cycle with 2000ppm hydrochloric acid, to remove any inorganic foulants. A higher dose of hydrochloric acid than normally recommended.

This highlights the need for proper coagulation control when dealing with pre-coagulation and ultrafiltration membranes, especially as excess coagulant can cause deterioration of the membrane performance but more significantly decrease the life span of the membrane.

In summary, to treat upland water that has a high humic content, the use of pre-coagulation with the Norit membrane produced the best performance in terms of treated water quality, with 90% DOC removal compared to 76% with the Zenon membrane. However, this is balanced by the fact that the Norit was susceptible to high levels of irreversible fouling. The Norit required chemical cleaning after 1.1 days continuous use, while the Zenon could last for 4.8 days before requiring cleaning.

As both membranes produced high quality water, the determination over the best option is a trade off between the higher water quality of the Norit or the reduced chemical cleaning with the Zenon.

In both cases, it should be noted that, if the coagulation regime is optimised with regard to coagulant dose, chemical cleaning is relatively straightforward. However, the control of coagulant is paramount as even small amounts of excess coagulant can have long-term implications into the cleaning regime and membrane life span, with iron fouling requiring elevated temperatures, which will increase the running costs of membrane filtration considerably.

The research has shown that the use of pre-coagulation to treat upland water is a viable option as long as the coagulation is optimised, however the research has also shown that the application is determined by the type of water, specifically the type of organics to be treated. This is highlighted by the use of coagulation and ultrafiltration to treat Draycote water. The water quality only improved to 53%, due the water containing a high percentage of organics that cannot be coagulated. For this type of water, alternative treatment methods have to be found.

Chapter 8

Enhanced coagulation technologies

8.1 Introduction

As was shown in the previous chapter, the removal of natural organic matter from Draycote Water is problematic. Although optimisation of coagulation followed by membrane ultrafiltration reduces the total organic content from 12 mg/L to 4.2 mg/L, this still leaves a significant amount of organic material in the treatment stream, with the potential of forming THMs. The current THM standard is >100μg/L at the customers tap, and although there is no limit on TOC content, there is a growing feeling amongst the water utilities that a TOC level of <2 mg/l will allow treatment works to meet THM compliance levels.

As part of an ongoing investigation into treatment process options aimed at reducing TOC levels, Severn Trent Water (STW) and ORICA Watercare Europe (OWE) agreed to conduct a trial at the Draycote WTW to evaluate the efficiency of NOM removal with MIEX®DOC pre-treatment and a downstream coagulation/DAF process. In this trial, the MIEX process was applied to raw water prior to any other treatment, with the downstream treatment was evaluated using a pilot DAF unit.

The aim of the trial was for the pilot plants to achieve an overall 75% removal of TOC; and produce water with <2 mg/l TOC after complete treatment (MIEX and DAF); individual process targets were:

MIEX = 45 – 50% DOC removal (45-50 % UV abs. reduction)
DAF = 20- 25% doc reduction (20-25 % UV abs. reduction)

As Draycote water has a high percentage of organic neutrals which are difficult to remove during normal operations, it was therefore proposed to implement a pre-ozone stage upfront of the MIEX process to alter the composition of the organics, and determine if pre-ozone was beneficial to MIEX performance. This involved jar test and pilot plant experiments.

8.2 Summary of experimental protocols

Materials and methods pertinent to this chapter were reported in **Chapter 4** of this thesis. In summary, MIEX®DOC resin was used in combination with dissolved air floatation to examine the reduction of DOC from Draycote water. The coagulant used in this chapter was ferric sulphate. pH correction of coagulation was with addition of hydrochloric acid. The experiments involved jar tests and pilot plant trials.

8.3 Results

8.3.1 Jar tests

To determine the mixing time required to remove organics from Draycote water, kinetic jar tests were conducted with virgin resin and regenerated resin from the fresh resin tank. This determines the mixing time required to reduce the organic content of the water, as well as highlight any difference in performance between the two types of resin (**Fig 8.1**). For the latter, the efficiency of the regeneration process at removing organic material from the resin is indicated.

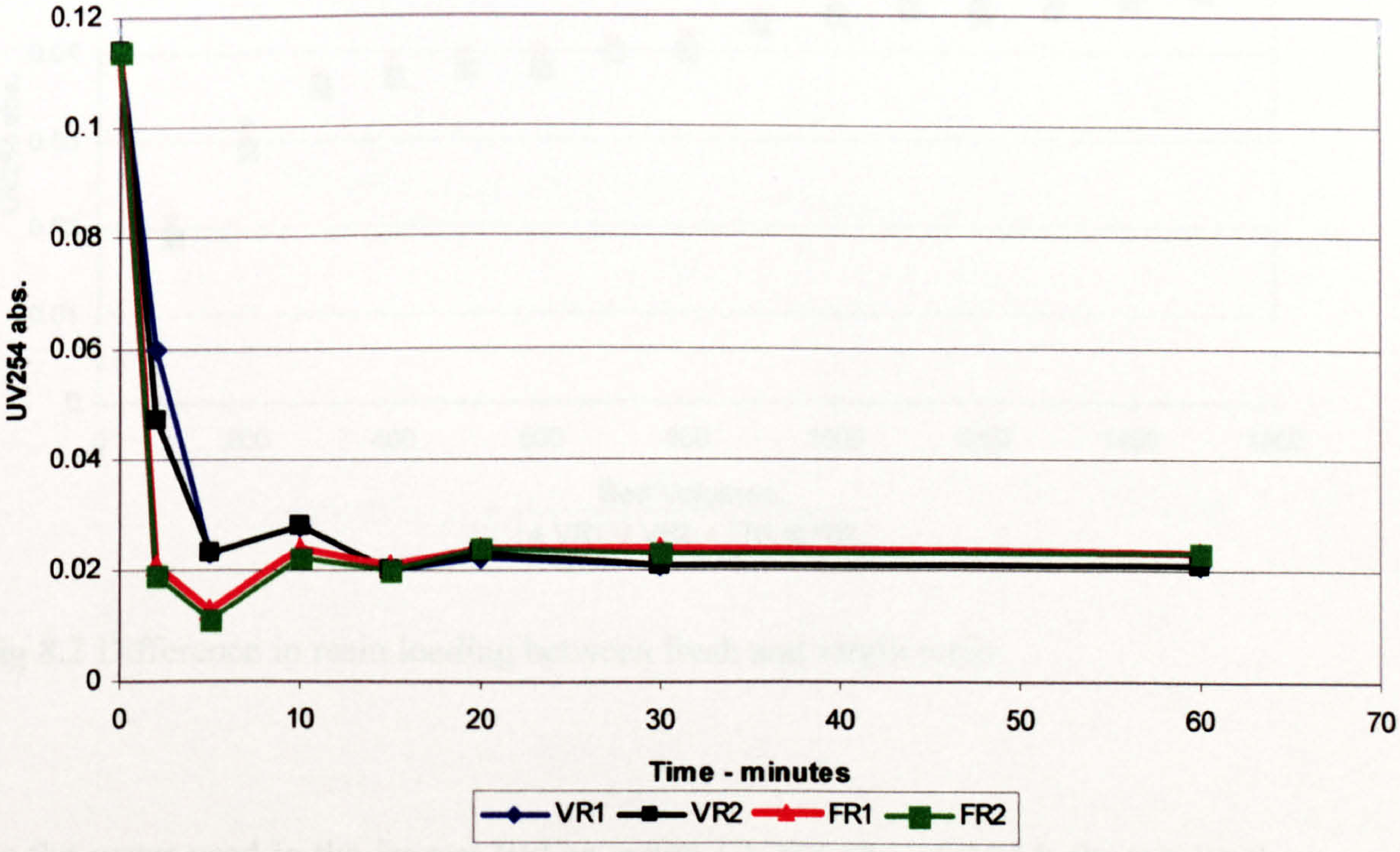


Fig 8.1 Difference in kinetic performance between virgin and regenerated resin

The results show that both resins obtain a ~80% reduction of UV254 absorption after 10 minutes, with only a small further reduction with extended mixing. This shows that the pilot plant contactors, with a 10 minute residence time, are adequate to treat this type of water.

The performance difference between the regenerated and virgin resin in the kinetic jar tests was slight, with the virgin resin outperforming the regenerated resin only after 10 minutes mixing, indicating that the regeneration process of the MIEX pilot plant is operated efficiently and the organics are virtually all removed by the brine. The fact that both resins obtain similar levels of performance after 60 minutes is a further indication that the regeneration process in the pilot plant is adequate.

The regeneration frequency of the MIEX process is determined by the amount of water that the resin can treat before resin performance deteriorates. To calculate the regeneration rate, loading jar tests were conducted (**Fig 8.2**).

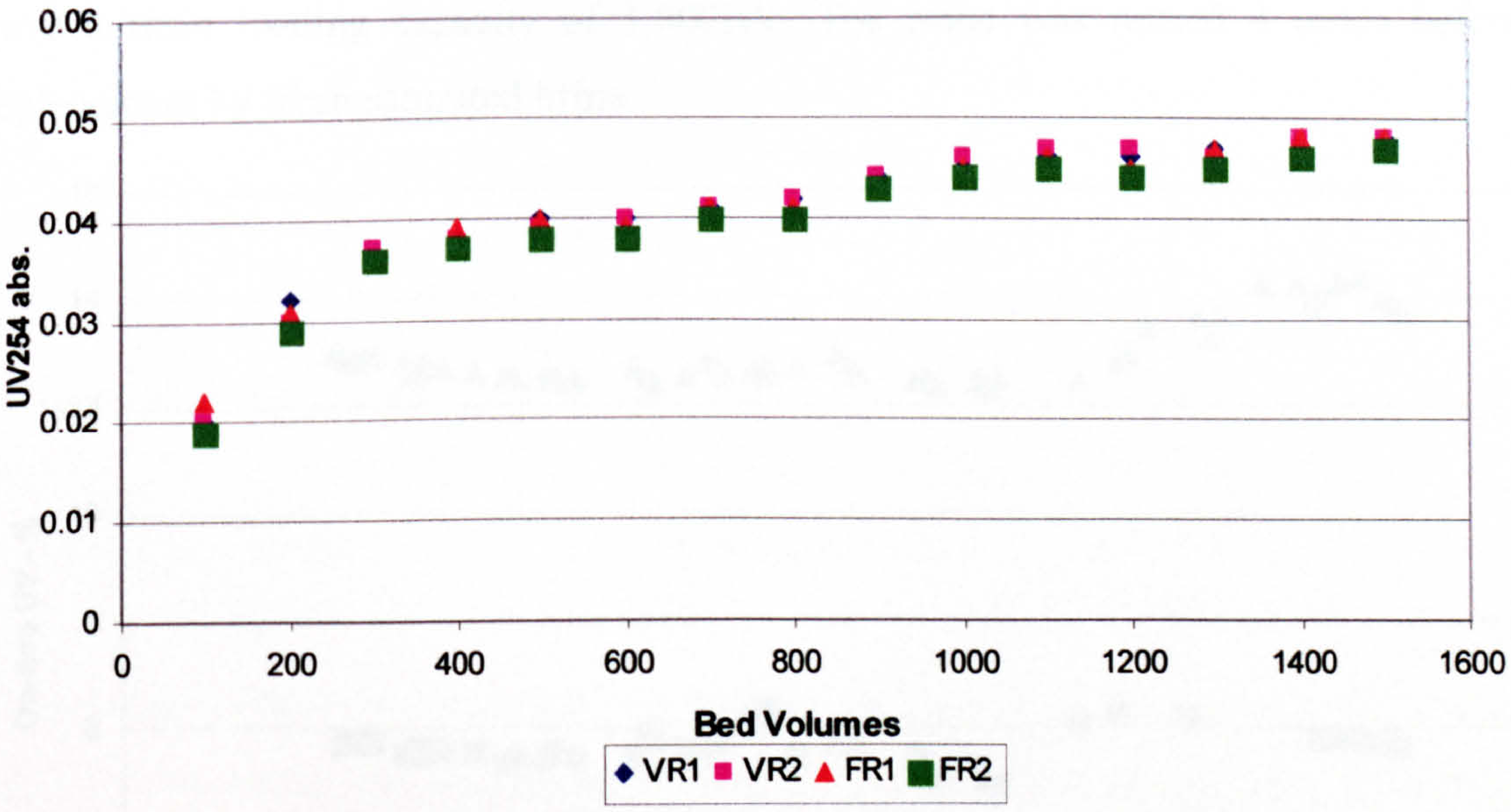


Fig 8.2 Difference in resin loading between fresh and virgin resin

As the water used in the jar test had an initial UV254 abs. of 0.114, the results show that even after 1500 BV, the resin is able to remove ~58% of the organic material. This is greater than the 45-50% UV abs. reduction target set in the trial objectives. However this result highlights the difference between the ability of the resin to remove organics (80% in kinetic test) and the actual removal efficiencies during a continual process. This shows that to evaluate MIEX properly loading jar tests or pilot trials are required.

As jar test results are notoriously more optimistic than pilot trials, the bed volume regeneration rate for the pilot rig was set at 1000BV to give a wider margin of error in resin performance and still meet the trial objectives. The fact that both resins perform virtually identically indicates that the regeneration process in the pilot plant is working correctly.

8.3.2 Pilot plant trial

Fig 8.3 shows the effect of MIEX resin on the removal of UV absorbing material, as determined by a series 7300 ABB online UV monitor. At the beginning of the trial the resin concentration in the contactor was 20 ml/L with a regeneration rate of 4 %. This gave a resin loading capacity of 1,000BV. The brine was reused 4 times before replacement by fresh saturated brine.

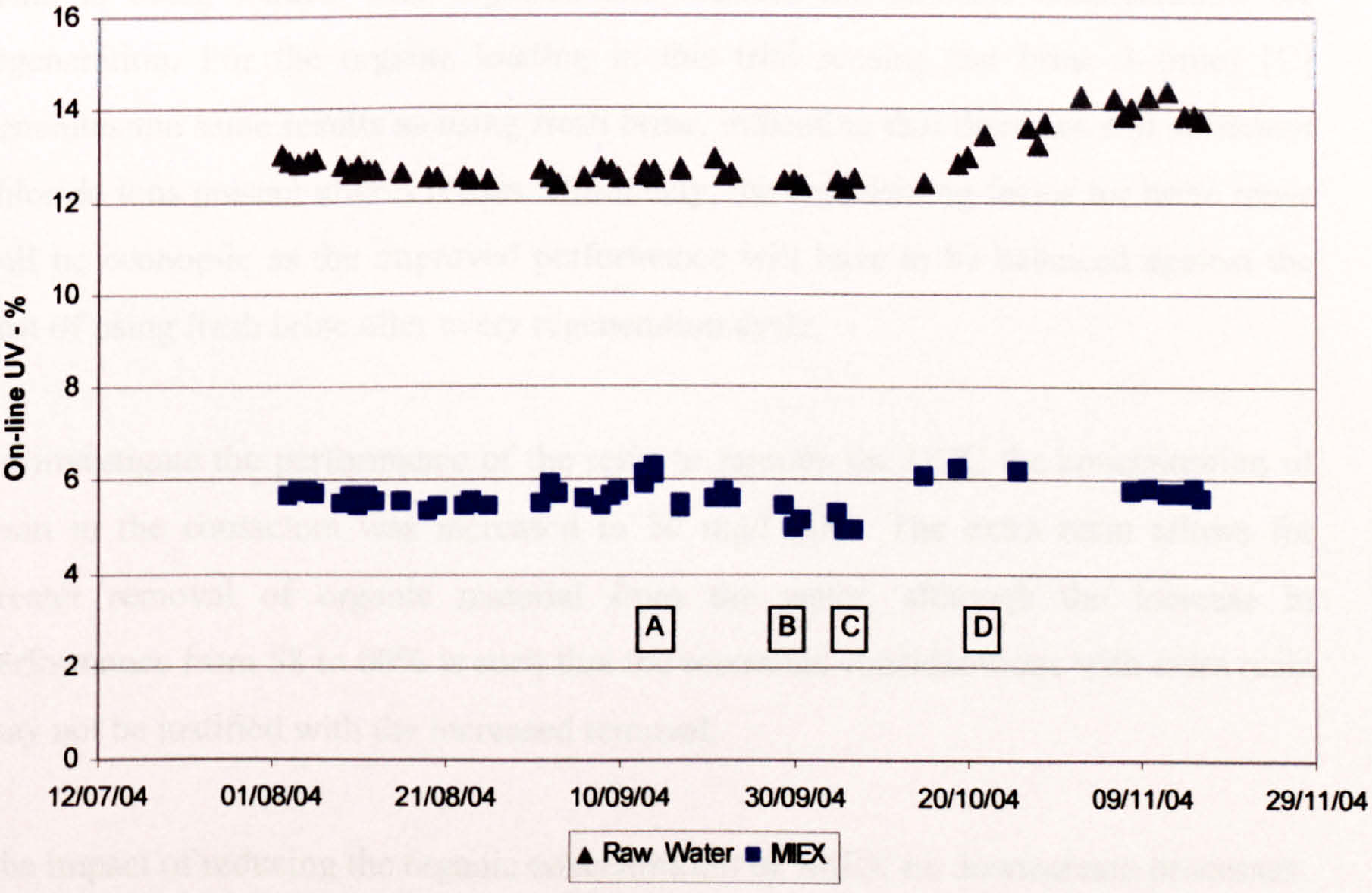


Fig 8.3 Removal of organics by MIEX resin – [A] represents no rinse cycle, [B] represents no brine reuse, [C] represents 3 brine re-usages and [D] represents 30 ml/L resin concentration.

The results show a consistent reduction in organic content throughout the trial, with a reduction in organics of ~56%. This figure varies when the operating parameters of the pilot plant are changed. At the beginning of the trial the resin is rinsed with treated water to remove any brine and concentrated organics left in the regeneration tank after brine draining. Depending on the organic loading it is possible to remove this step. The results [A] indicate that removing the rinse cycle increases the level of organics present in the treated water. This is due to concentrated organics remaining in the resin, which are then released in the fresh resin tank and ultimately the level of organics in the contactors. A rinse cycle would flush these organics from the resin during the regeneration process and as the results show, for this type of water a rinsing cycle is required.

To determine the ability of the brine to regenerate the resin the number of times the brine was reused was reduced [B]. By using fresh brine with every regeneration, the maximum number of chloride ions is available for exchange with the DOC. The slight increase in performance indicates that the number of brine reuses is too high, as the brine is being loaded with organics and reduces the chloride concentration for regeneration. For the organic loading in this trial reusing the brine 3 times [C] generates the same results as using fresh brine, indicating that there are still sufficient chloride ions present after 3 reuses. Ultimately, the determining factor for brine reuse will be economic as the improved performance will have to be balanced against the cost of using fresh brine after every regeneration cycle.

To investigate the performance of the resin to remove the DOC the concentration of resin in the contactors was increased to 30 mg/l [D]. The extra resin allows for greater removal of organic material from the water, although the increase in performance from 58 to 60% is such that the economic considerations with extra resin may not be justified with the increased removal.

The impact of reducing the organic concentration by MIEX on downstream processes was also investigated. The MIEX treated water was fed into the DAF pilot plant and on line UV measurements taken **(Fig 8.4)**.

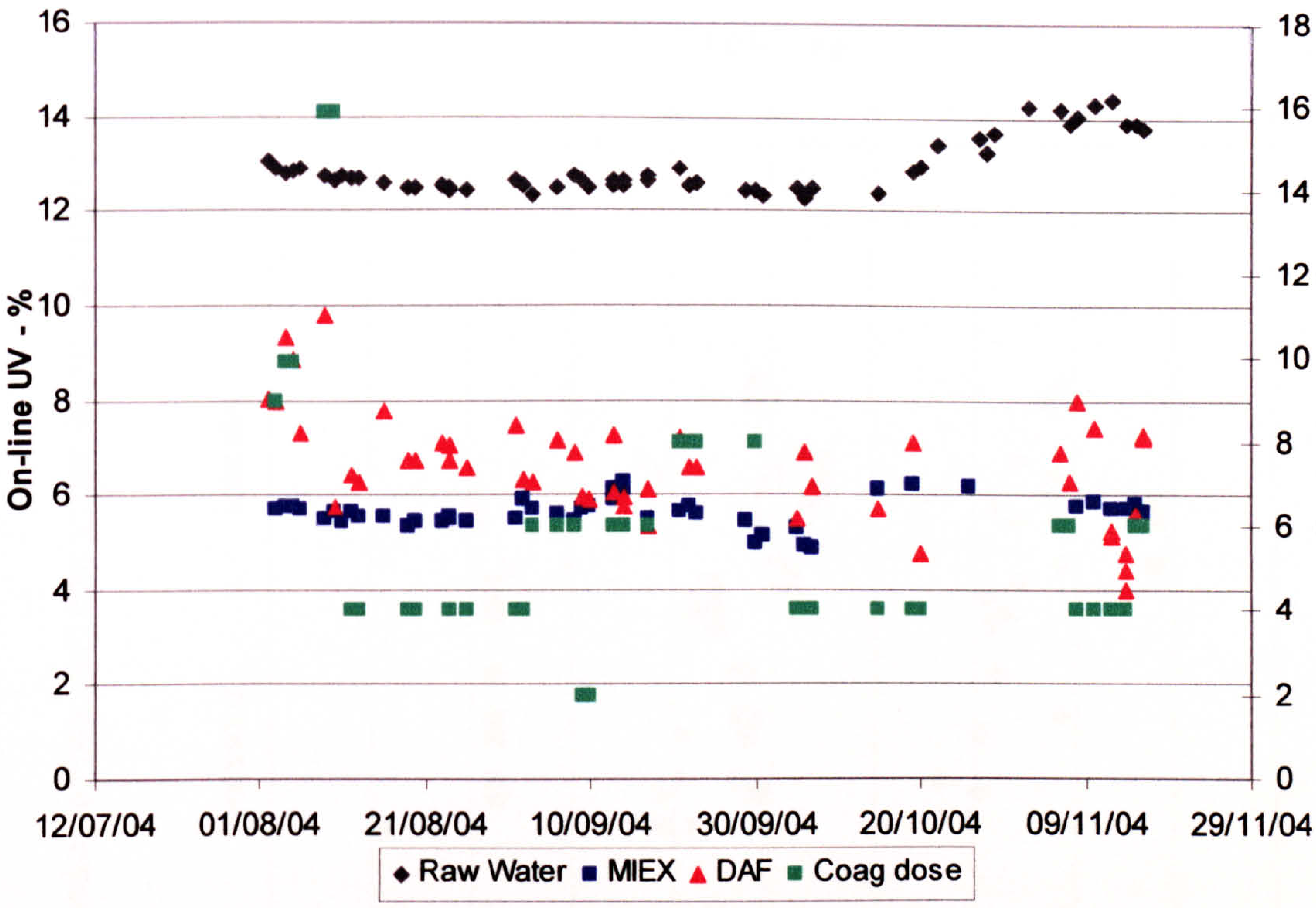


Fig 8.4 online UV measurements of MIEX then DAF treated water and corresponding DAF coagulant dose

The results show an increase in online UV for the DAF treated water. This is surprising, as the DAF would be expected to further reduce the organic content of the water. The reason for this discrepancy is that the coagulant used was ferric sulphate and that the DAF process left excess iron in solution which affected the UV readings. As online UV cannot be used to accurately determine organic removal, TOC measurements were conducted. As the samples were filtered though 0.45μm filters, the organic content can be referred to as DOC. **Fig 8.5** shows the reduction in DOC by MIEX and then further by DAF, as well as the corresponding coagulant dose.

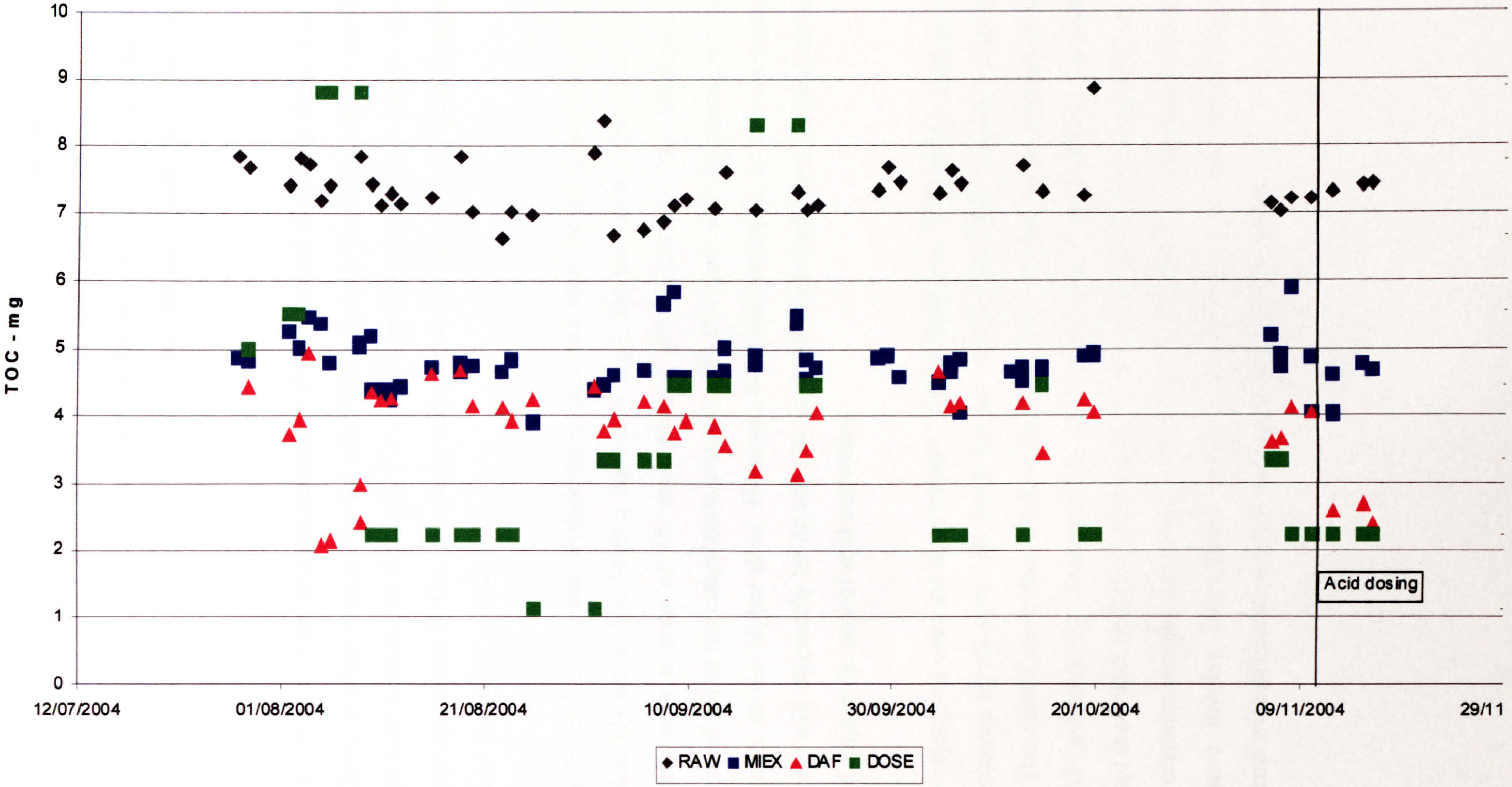


Fig 8.5 Reductions in TOC by MIEX then DAF and corresponding DAF coagulant dose (including period of pH acid dosing)

The results in **Fig 8.5** show that the MIEX resin removes on average 35% of the DOC content, which is then further reduced by the DAF process. The amount of DOC removed by the MIEX is fairly constant throughout the trial, while the amount of DOC removed by the DAF is dependant on the pH and dose of the coagulation process. At the start of the trial no pH correction was used, with the pH set by the amount of ferric added.

The results show that the greatest removal of DOC was with the higher ferric dose. 15 mg/l of ferric sulphate reduces the doc after MIEX by a further 39%, while a low dose of 4 mg/l only reduces the DOC by 7-10%. As there was no pH correction, it was difficult to determine if this reduction was due to the amount of ferric hydroxide available or the pH of coagulation.

Towards the end of the trial hydrochloric acid was used for pH correction with the coagulation pH set at 5.8. With a dose of 4 mg/l, the reduction in DOC was 39%, comparable with a dose of 15 mg/l without pH correction. This highlights the importance of pH in the coagulation process, with the lesser dose producing the same water quality as the higher dose. However, the implementation of pH correction in this process will ultimately be decided by economic considerations; the cost of extra coagulant against the cost of acid correction.

The trial objectives were set as an overall DOC reduction of 75%, MIEX reducing the organic content by 45-50% with DAF further reducing the DOC content by 20-25% (2mg/l). The results show that MIEX reduced the DOC content by an average of 35% with DAF reducing the level to 71%, just above the 2 mg/l target. To further understand the MIEX and DAF performance, a detailed analysis was conducted on the types of organics present before and after treatment (**Table 8.1**). The results for DAF performance involve coagulation without pH correction, as the results for the experiments with pH correction are pending at the time of writing.

Table 8.1 Characterization of TOC content of raw water before and after treatment by MIEX and DAF

			DOC VALUES	
	TOC	DOC	hydrophobic	hydrophilic
	Ppb	ppb	HOC - ppb	CDOC - ppb
Raw water (1)	6428	6096	158	5938
Miex	4100	3912	190	3722
DAF – 4mg/l	3890	3510	108	3402
Raw water (2)	6707	6248	385	5863
Miex	4471	4183	294	3889
DAF – 8mg/l	3695	3218	132	3085
DAF 15mg/l	3444	3150	241	2908

	HYDROPHILLIC FRACTION				
	Polysaccharidic	Humics	Building Blocks	neutral Amphiphilics	LMW acids
	Ppb	ppb	ppb	ppb	ppb
Raw water	750	2744	1311	1089	45
Miex	691	958	1219	854	0
DAF – 4mg/l	461	917	1229	796	0
Raw water	802	2798	1254	975	34
Miex	849	949	1256	835	0
DAF – 8mg/l	408	750	1164	762	0
DAF 15mg/l	326	663	1134	786	0

NB Analysis (1) and (2) conducted on different days

The raw water results show a high proportion of building blocks and neutral amphiphilics, which are not normally removed by flocculation due to their low molecular weight and weakly charged hydrophilic or slightly hydrophobic nature. This explains the MIEX performance in reducing DOC; the resin is designed to remove charged particles but the humics only compose ~40% of the total DOC. The resin removes over 66% of the charged organics, with DAF further reducing the level by 30% at the highest dose. The removal of the building blocks and neutrals is poor, although there is some reduction, which is possibly due to enmeshment by the growing flocs.

The levels of polysaccharides in MIEX treated water are also high, and can be seen by algae growth in the contactors (**Fig 8.6**). This may be because the contactors and settler tanks are made of clear Perspex allowing, light to aid the growth of the algae. Enclosed contactors and the use of a finer pre-filter may reduce this problem.

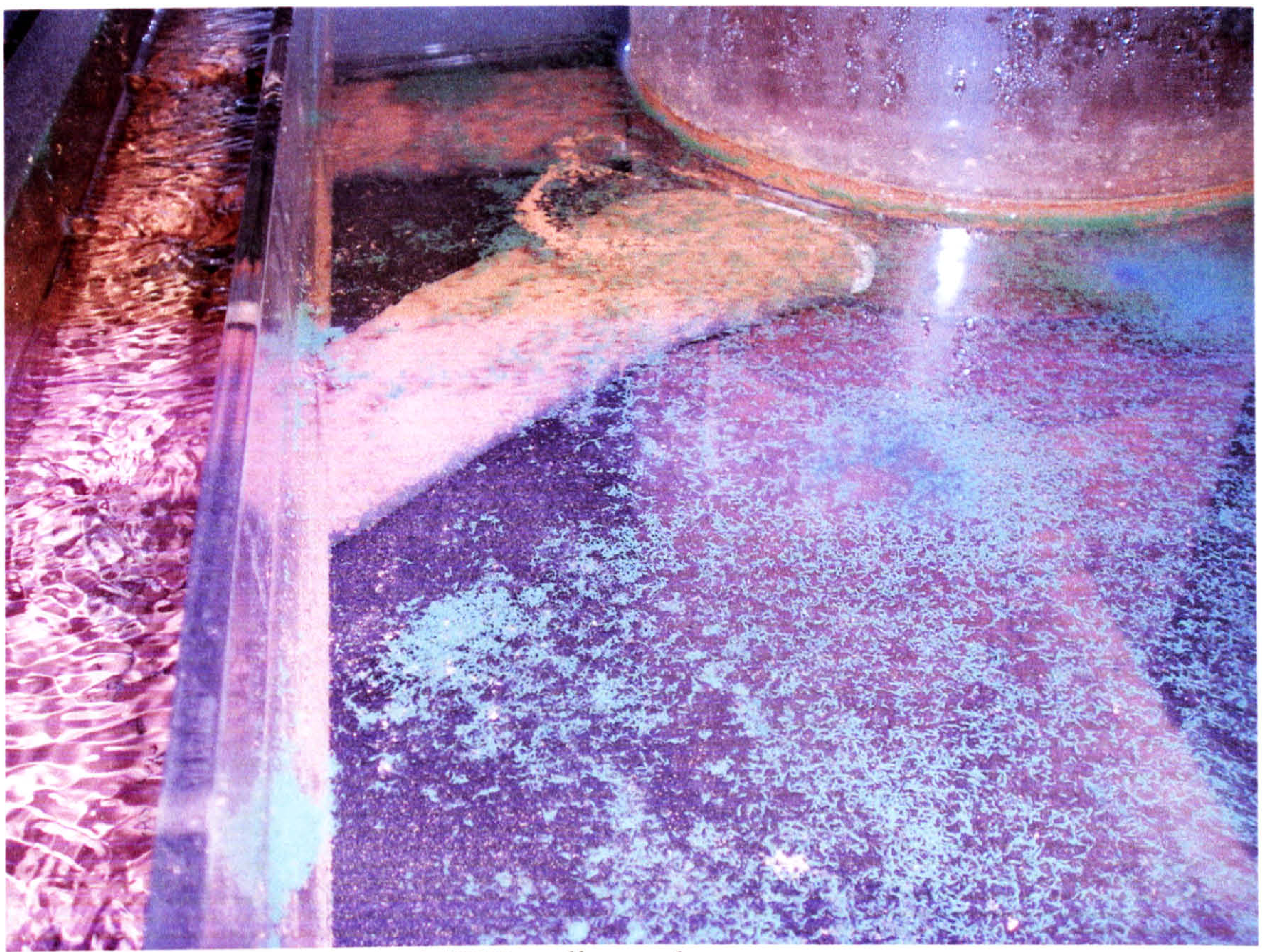


Fig 8.6 Algae growth in the MIEX settling tank

Although MIEX performed consistently, reducing the DOC content by an average of 35%, and the DAF reduced the level further; there is still a significant proportion of NOM in the treated water. To improve the treatment of Draycote water, a solution has to be found which will reduce the neutral component of the NOM. One solution may be to use ozone to charge the particles, allowing them to be removed by either MIEX or DAF.

8.3.3 Ozone pre-treatment

Kinetic Jar Tests

Fig 8.7 shows the results from the kinetic jar tests to determine what effect, if any, ozone had on the removal of organics. In this experiment 10 ml of resin was used to treat 1 litre of raw water; 1 litre of raw water pre-treated with 2ppm ozone and 1 litre of raw water pre-treated with 4ppm of ozone.

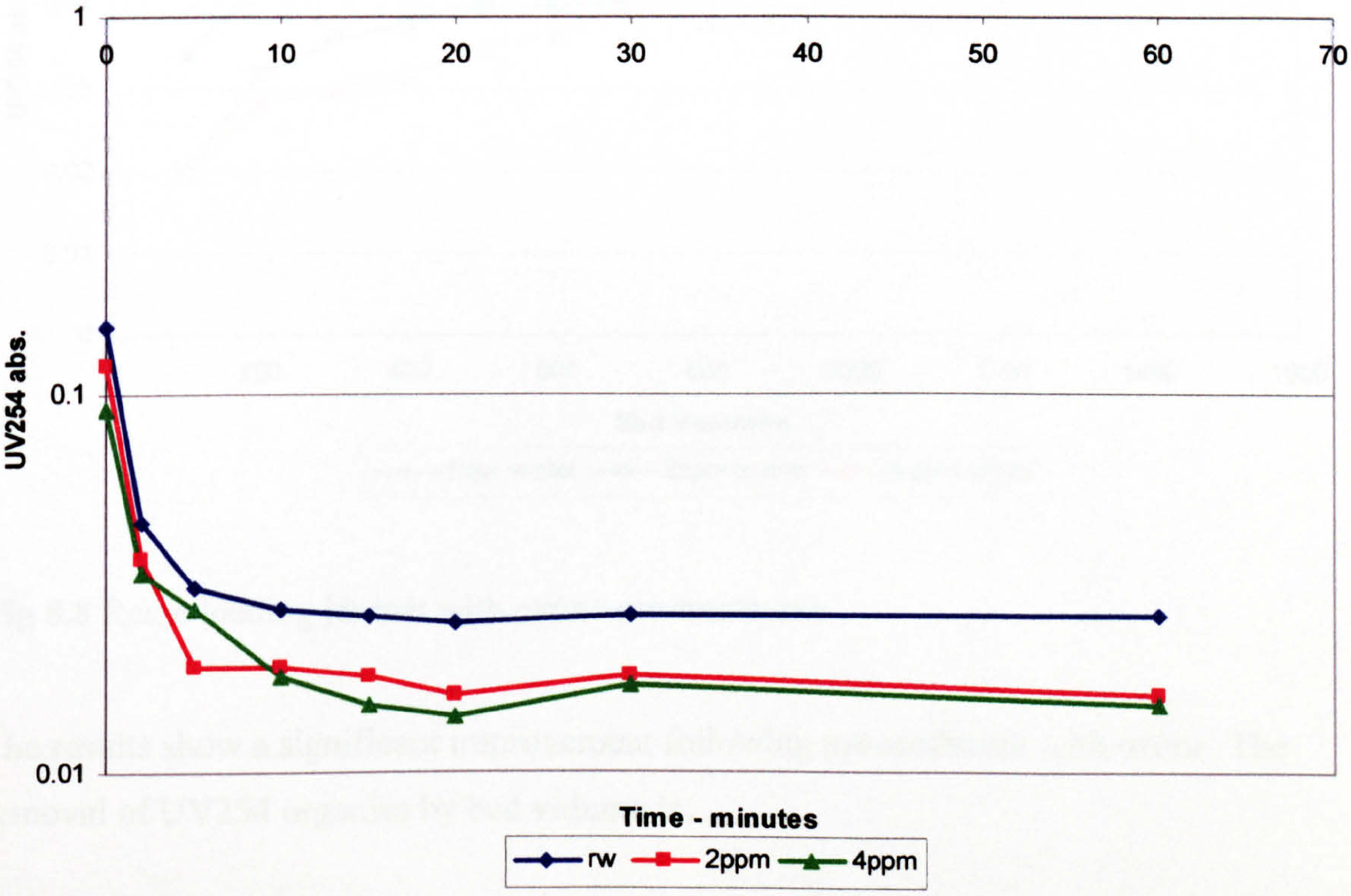


Fig 8.7 Reduction in UV254 levels during Kinetic jar test

The results shown in **Fig 8.7** indicate that the introduction of ozone before MIEX treatment has a beneficial effect on UV254 abs. removal. The improvement in UV254 removal with the addition of ozone is ~10% after 10 minutes mixing. The UV254 of the raw water was 150 abs. units, with a reduction to 0.12 abs. and 0.091 abs. with 2ppm and 4ppm ozone respectively. Although the UV254 levels are reduced this is not sufficient to indicate improved performance in DOC removal. As previously shown, a significant proportion of Draycote water is neutral organics. Further analysis is required.

8.3.5 Resin loading Jar Tests

Fig 8.8 shows the capacity of the resin to adsorb organic material pre-treated with 2ppm ozone, as well as with 4ppm ozone.

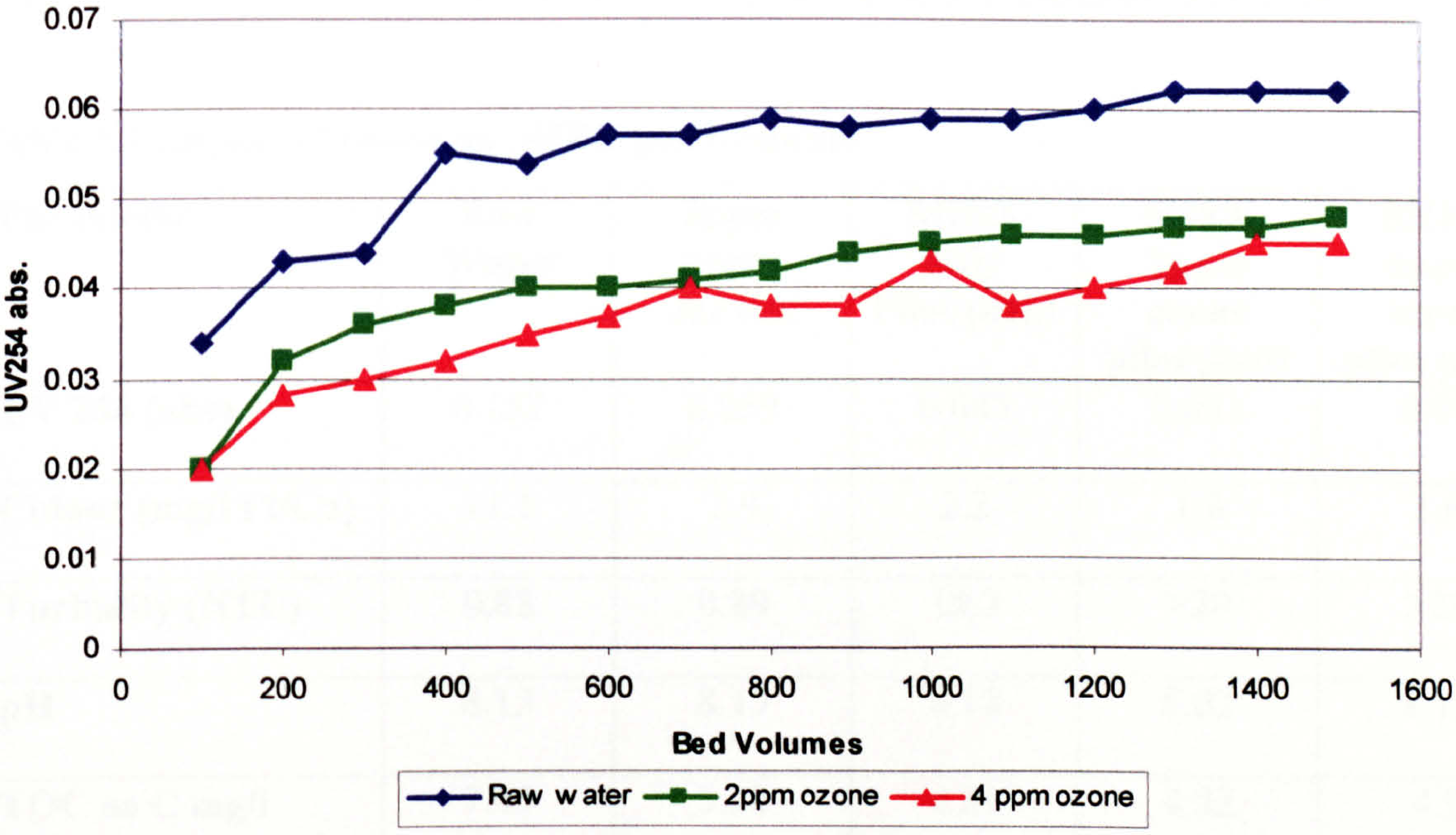


Fig 8.8 Resin loading jar test with ozone pre-treatment

The results show a significant improvement following pre-treatment with ozone. The removal of UV254 organics by bed volume is:

BV	MIEX	2ppm ozone	4ppm ozone
500	73.0%	76.0%	80.0%
800	69.0%	74.0%	78.0%
1000	64.6%	73.0%	77.0%
1200	64.0%	72.7%	76.6%
1500	62.0%	70.8%	74.6%

The performance is similar to the kinetic jar tests, with a ~10% improvement with 2ppm ozone, and a further ~4% improvement after increasing the ozone to 4ppm. All the treatment results achieve the pilot plant trial objectives for a UV254 reduction of 45-50%. It should again be noted that changes to organics by ozone make UV254 results suspect, and DOC analysis is required to validate DOC performance.

Laboratory analysis was conducted by Severn Trent on the raw water and the 2ppm jar test (1500 bed vols.), for comparison with the MIEX pilot plant results (**Table 9.2**). The raw water going into the MIEX pilot plant was pre-treated with 2ppm and 4ppm ozone. It should be noted that limitations in the ozone equipment meant that only 50% of the water entering the MIEX process had been pre-treated with ozone.

Table 8.2 Impact of ozone on MIEX performance

Parameters	**Raw Water**	**2ppm ozone Jar test**	**MIEX only Pilot plant**	**MIEX 2ppm ozone pilot plant**	**MIEX 4ppm ozone pilot plant**
UV 254 (abs)	0.157	0.059	0.085	0.081	0.07
Colour (mg/l Pt/Co)	11.1	2.9	2.2	1.8	1.6
Turbidity (NTU)	0.88	0.89	19.3	>20	>20
pH	8.13	8.15	8.12	8.02	8.15
TOC as C mg/l	7.45	5.08	4.81	4.92	4.9
Total Aluminium µg/l	19	23	120	152	14
Total Iron µg/l	23	101	217	338	205
Total manganese µg/l	3	5	3	3	3

The pilot plant results mirror those obtained by the jar test in terms of UV 254 abs, with a slight increase in removal with ozone against MIEX alone. As only half the water was treated with ozone, the reduction is ~45% compared to 62% with the jar tests.

However, the most significant results are the TOC values (Severn Trent labs filter the samples (0.45 microns) before analysis, so the TOC can be considered as DOC). The MIEX pilot plant was run at a resin loading capacity of 700 bed volumes, which the jar tests indicated a DOC reduction of 31%; the DOC reduction with the pilot plant was ~35%. The addition of ozone was intended to charge the neutral organics in the water and increase the DOC removal over MIEX alone. However the TOC results taken in conjunction with the UV 254 abs values, indicate that the ozone, rather than charge the neutral organics, actually broke down the large molecular weight humics (as indicated by the reduction in UV254 after addition of ozone). Without TOC fractionation, it is difficult to comment on the type of organics present after the addition of ozone. However, as the MIEX pilot plant out performed the ozone pre-treated MIEX pilot plant results, it can be speculated that the ozone broke down the humics that MIEX can target, and increased the amount of organic building blocks.

8.4 Conclusions

MIEX performs consistently, reducing the TOC levels by ~35%, with DAF further reducing the TOC levels to a total of ~70% (2.3mg/l DOC), although still not below the target of 2 mg/l. This is significantly lower than the results published on MIEX performance, where DOC removal is nearer 70% (see **Chapter 2.10**). This difference is due to the published work being conducted with kinetic jar tests. As stated before kinetic tests allows investigation into the removal efficiency of organics by MIEX but does not give any indication as to the removal efficiencies in a continuous loading process. For this to happen, loading jar tests or pilot trial work needs to be conducted.

The DAF performance is linked with the pH of the coagulation process, and as a consequence DAF improves greatly when there is pH correction. However, there is still a significant proportion of NOM in the treated water. Initial analysis shows this to be the hydrophilic neutral component of NOM (which cannot be flocculated out).

Although there is still a 2.3 mg/l DOC in the treated water, this is still significantly lower than the 4.3 mg/l achieved when pre-coagulation with ultrafiltration (see **Chapter 7.3.4**) was used to treat Draycote water. This may be due to MIEX removing the low molecular weight organics that coagulation along does not remove, as shown by Humbert H. et al (2005).

Although this work indicates that MIEX treatment upfront of DAF is the more viable treatment option. To further improve the DOC reduction levels, the use of ozone to pre-treat the water before MIEX was investigated.

The results show that the use of ozone to aid the removal of organic material from Draycote water in fact causes deterioration in MIEX performance. Although both jar tests and pilot plant results showed a significant reduction in UV254 abs, the actual DOC values remained high. The results show that the addition of ozone, rather than aid the process by charging the neutral organics was breaking down the humic acids that the MIEX process targets.

The time scale involved for these results limited the amount of testing and, although the results were unfavourable, it may be that the amount of ozone present was too high and that reducing the amount of ozone present may charge the neutrals rather than break down the humic acids. Alternatively a better option may be treating the water with MIEX to remove the charged organics present and then treating the water with ozone and then GAC to remove the remaining organics. However, based on the current results the addition of ozone is not a satisfactory aid.

Another area of research that could be explored is in the choice of MIEX resins. The resin used in this trial was anionic based and was shown to remove the majority of negatively charged particles. The fact that the remaining NOM is referred too as neutral organics may be a misnomer, as the particles are just very weakly charged. Sharp, E. L., S. A. Parsons, et al. (2005) stated that the hydrophobic NOM fractions have a significantly higher charge density than the hydrophilic NOM fractions, whereas the hydrophilic non-adsorbed fraction has a negligible charge density. It may be that the organics remaining, after treatment of Draycote water, have a different charge, albeit weak, and that combining the anionic resin with a cationic resin in series may be an answer to the problematic Draycote water. Further research is required.

Chapter 9

Conclusions

As this report is based on the impact pre-coagulation has on ultrafiltration membrane performance, the optimisation of coagulation conditions represents the conditions that provide the greatest removal of NOM in the shortest possible time, while allowing the flocs to grow large enough to remove any excess iron.

The pH of coagulation greatly affects the growth of flocs. Although flocs are produced over the range of pH values, there is a significant improvement in performance at the optimum pH. The results show that for ferric sulphate, the optimum pH value for coagulation was 4.8; for ferric chloride the optimum pH value was 5.0; and for alum the optimum pH value was 6.7.

At the optimum pH, the amount of coagulant available greatly affects the coagulation performance As the optimum coagulant dose is generally associated with a near zero zeta potential, the results indicate that when each coagulant is operated at its optimum, ferric sulphate outperforms both ferric chloride and alum. The difference between the two ferric salts is slight, with ferric sulphate producing the largest, most stable floc. Alum performs poorly, with more than double the mass of coagulant needed to reach the performance of the ferric salts.

Manipulation of the mixing regime during orthokinetic flocculation allows control of the final floc size. By increasing the initial rapid mixing speed, the rate of growth during the slow mixing period is affected. A high shear rate ($447s^{-1}$) induces greater particle collision and micro-floc formation, allowing an increased rate of growth during slow mixing. At the higher shear rate, all the coagulant is dispersed and formed into flocs, which are larger than 8 microns, after 60 seconds of rapid mixing; however, there still remains dissolved iron present. A mixing regime of 60 seconds rapid mixing (shear rate $G = 447\ s^{-1}$) followed by 3 minutes slow mixing (shear rate G

= 20 s^{-1}) is required for flocculation of the NOM and adequate enmeshment and removal of excess iron.

The seasonal variations in temperature have a direct effect on the orthokinetic flocculation. As the temperature decreases, so to does the flocculation performance. Results show that the initial coagulation process is not greatly affected by temperature; however, temperature does affect the rate of flocculation. The lower temperature causes the formation of smaller and denser flocs. The reduced size of the flocs diminishes the performance of 'sweep flocculation', as there is a reduced surface area to enmesh the particles. This has a significant impact on the removal of the excess iron fraction. At 20.0°C the excess iron is removed by enmeshment after 4 minutes. As temperature falls so the time required to remove the iron increases. At 4°C iron remains in solution even after 14 minutes.

Particulates in water aid coagulation as they provide nucleating sites on which flocs can form and grow. Low turbidity waters lack these seeding points and although at high temperatures this is not a problem; at low temperatures this lack of particulates can hinder the coagulation process. The addition of lime for pH correction can remedy this problem due to its colloidal nature.

The results show that the removal of iron at low water temperatures, when lime and coagulant are added together, is improved when the pH is increased to 4.9. However, the improvement is slight with over 0.12 mg/l Fe^{3+} still remaining in solution. When lime is added before the coagulant, the greater floc growth increases the removal of excess iron through enmeshment by the larger floc, with only 0.04mg/l Fe^{3+} left in solution after 14 minutes of mixing. Further research is required to determine if the removal of excess iron at low temperatures can be improved below this level.

Experiments conducted with the optimised coagulation regime and a Norit hollow fibre ultrafiltration membrane, operated in dead-end mode, leads to significant fouling. The type of fouling involved with this Norit membrane module is determined by the coagulation regime. With a longer mixing time, the large flocs formed block the hollow fibres and performance deteriorates, such that frequent chemical cleaning is required. By reducing the mixing time, the membrane performance improves, although the fouling mechanism changes to surface fouling by organic iron species. Chemical cleaning with sodium hydroxide followed by citric acid produces the best recovery rates with 100%.

The results for the submerged Zenon ultrafiltration membrane also indicated membrane fouling, when the coagulation regime was optimised for NOM reduction and iron removal (1 minute of rapid mixing followed by 4 minutes slow mixing). Although the fouling was less than the use of pre-coagulation with a Norit UF membrane, the levels were still significant. When the slow mixing time was increased to 8 minutes the fouling reduced remarkably

With the correct coagulant dose and mixing regime, the fouling of the Zenon membrane is mainly due to NOM, and can be remedied by normal chemical cleaning (hydrochloric acid and sodium hypochlorite). However, this does not remove the iron left on the membrane by overdosing. The results have shown that for the cleaning solutions to react with the fouling layer, elevated temperatures are required.

The results from the cleaning study, taken in conjunction with the membrane filtration experiments show that the fouling of the membrane is due to a combination of organic material and iron. The fouling exacerbated if an incorrect coagulation dose is applied.

Initial research into the use of zeta potential as a coagulant control sensor was encouraging. The results have shown that zeta potential can be used to consistently detect changes in coagulation conditions. The variation in measurements for all conditions was only ± 0.7 mv. Although in the early stages of development, the use of zeta potential as an in-line coagulant dosing control shows promise.

This report also investigated the efficiency of NOM removal with MIEX®DOC pre-treatment and a downstream coagulation/DAF process. In the trial, MIEX performed consistently, reducing the TOC levels by ~35%, with DAF further reducing the TOC levels to a total of ~70% (2.3mg/l DOC). DAF performance was linked with the pH of the coagulation process, and as a consequence DAF improved greatly when there was pH correction.

Although there was still 2.3 mg/l DOC in the treated water, this was still significantly lower than the 4.3 mg/l achieved when pre-coagulation with ultrafiltration was used to treat Draycote water. This indicates that MIEX treatment upfront of DAF is the more viable treatment option. To further improve the DOC reduction levels, the use of ozone to pre-treat the water before MIEX was investigated.

The results show that the use of ozone to aid the removal of organic material from Draycote water in fact causes deterioration in MIEX performance. Although both jar tests and pilot plant results showed a significant reduction in UV254 abs, the actual DOC values remained high. The results show that the addition of ozone, rather than aid the process by charging the neutral organics was breaking down the humic acids that the MIEX process targets. Although the results were unfavourable, it may be that the amount of ozone present was too high and that reducing the amount of ozone present may charge the neutrals rather than break down the humic acids. However, based on the current results the addition of ozone is not a satisfactory aid.

Before implementing a treatment process a complete analysis of the raw water should be conducted for TOC and inorganic content. More importantly fractionation of the natural organic matter should be conducted, as the organic species present dictate the most efficient method of treatment.

It can be concluded that the optimum coagulation conditions in conventional water treatment are not always the optimum conditions for coagulation with ultrafiltration treatment and the unconventional coagulation conditions can be much more effective, than the conventional ones, in the context of membrane filtration, depending on the raw water characteristics.

In summary, the research conducted in this report has shown that an integrated coagulation –membrane filtration process is a viable option for the treatment of low turbidity waters containing high levels of NOM. However, it should be noted that the efficiency of the treatment is dependant on the type of raw water; coagulation parameters and membrane configuration. The research also showed that when the type of raw water was not suitable for pre-coagulation with ultrafiltration membranes, MIEX®DOC pre-treatment with a downstream coagulation/DAF process provided a viable alternative treatment option.

Chapter 10

Recommendations for future work

The next important step in developing the use of pre-coagulation with ultrafiltration membranes is to further investigate the optimisation of the coagulation process. The work in **Chapter 6** has shown that excess coagulant, particularly ferric based, cause significant problems in down stream processes. The role of alternative coagulants (polymer based) should be investigated further. The impact of these polymeric coagulants on coagulation at low temperatures should be examined.

Although in the early stages of development the use of zeta potential as an in-line coagulant dosing control shows promise (**Chapter 6**). The ultimate aim is to develop a computerised control system, however, more research is first required to determine whither zeta potential can be used with different coagulants and different types of water.

The work in **Chapter 7** has shown that the hollow fibres of the Norit membrane are susceptible to fouling when pre-coagulation is used; the membrane fibres had an internal diameter of 0.8mm and were prone to blocking. It would be advantageous to conduct experiments with a Norit membrane that has a larger internal diameter to eliminate this problem, particularly as the cleaning study conducted, showed that the Norit membrane could cope with higher concentrations of cleaning chemicals and produce 100 % recovery rates even when there was coagulant overdosing.

The success of the Zenon membrane to treat upland water (**Chapter 7**), when the coagulation regime had been optimised for membrane performance has justified an investigation with a larger scale treatment plant. The next step would be to increase the membrane module size and flow rate capacity to determine if pre-coagulation and submerged ultrafiltration membranes could be a viable option for the treatment of low turbidity, high NOM upland waters

In **Chapter 8**, both jar tests and pilot plant results showed that combining ozone with MIEX has a significant reduction on UV254 abs. levels, although actual DOC values remained high. The results show that the addition of ozone, rather than aid the process by charging the neutral organics was breaking down the humic acids that the MIEX process targets. It may be that the amount of ozone present was too high and that reducing the amount of ozone present may charge the neutrals rather than break down the humic acids. Alternatively a better option may be treating the water with MIEX to remove the charged organics present and then treating the water with ozone and then GAC to remove the remaining organics. Another area of research that could be explored is in the choice of MIEX resins. The resin used in this trial was anionic based and was shown to remove the majority of negatively charged particles. It may be that the organics remaining, after treatment of Draycote water, have a different charge, albeit weak, and that combining the anionic resin with a cationic resin in series may be an answer to the problematic Draycote water. Further research, particularly fractionation, is required into the changes in organic makeup that ozone has as well as the role of cationic resins.

Finally, a word on the long-term development of hybrid clarification-filtration treatment processes. It would be worthwhile for any researcher in the field to discover a viable treatment method for removing neutral organic material, a main source of problems in the water industry; particularly if a method could be found to enable a charge to be introduced onto these neutral organics.

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A.2 Summary of experimental protocols

Materials and methods pertinent to this chapter were reported in **Chapter 4.4** of this thesis. Coagulation experiments were conducted with ferric chloride, ferric sulphate and alum on raw water from Bamford WTW and Draycote WTW. The research involved optimisation of pH, coagulant dose, mixing regime and the effect of temperature on coagulation performance.

A.3 Results

A.3.1 Coagulation pH - Bamford

Standard jar-test experiments were conducted with ferric sulphate, ferric chloride and alum on Bamford water. **Fig A.1** shows the reduction of UV254 abs. at various pH values when a ferric sulphate dose of 3 mg/l Fe^{3+} was used. The results show that for ferric sulphate, the optimum pH value for coagulation was 4.8.

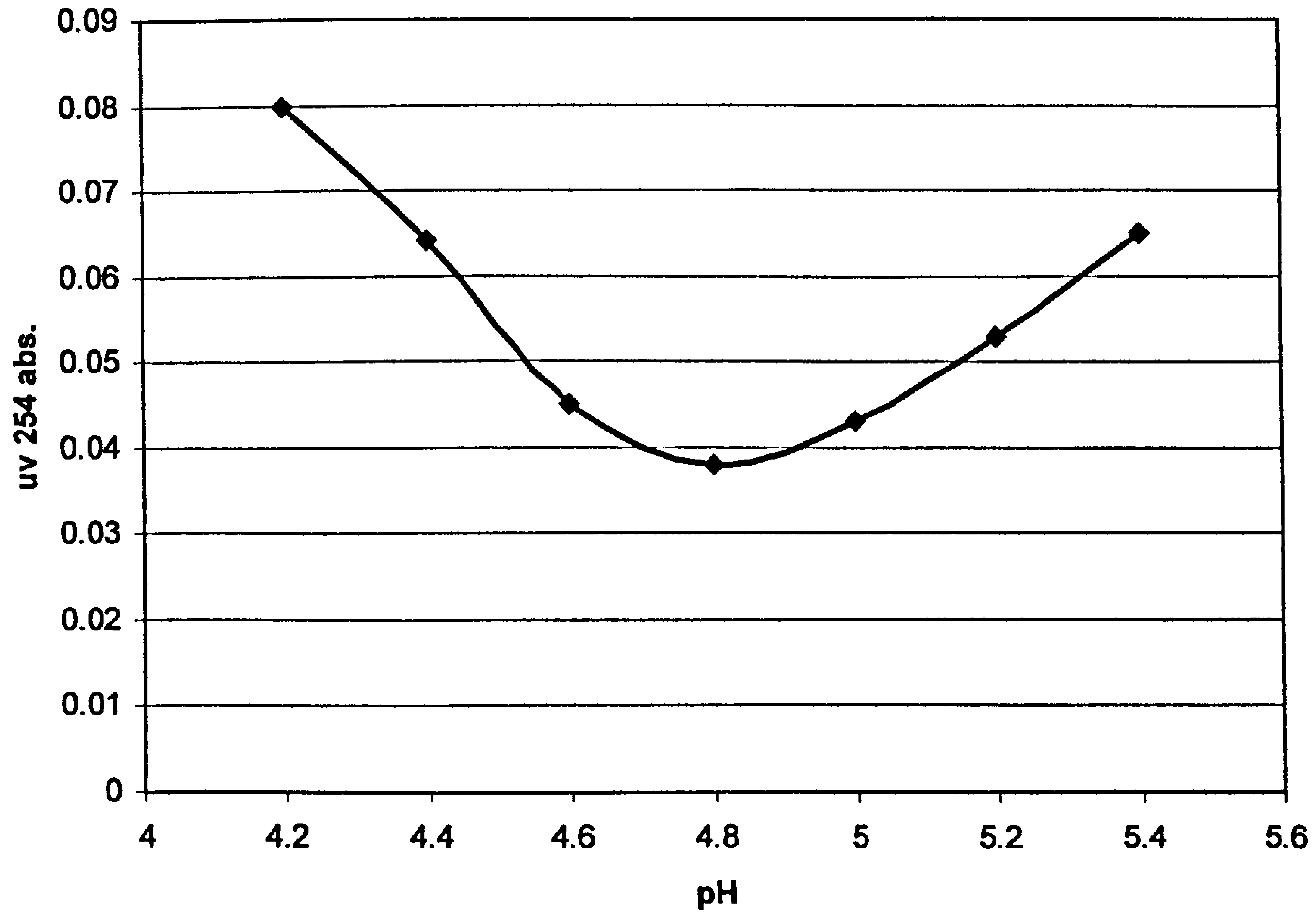

Fig A.1 Impact of pH on ferric sulphate coagulation

To compare the optimum pH values for different ferric coagulant salts, ferric chloride was used. With a constant coagulant dose of 3 mg/l Fe^{3+}, jar-tests were conducted with varying pH values (**Fig A.2**). The results showed that, for ferric chloride, the optimum pH value for coagulation was 5.0.

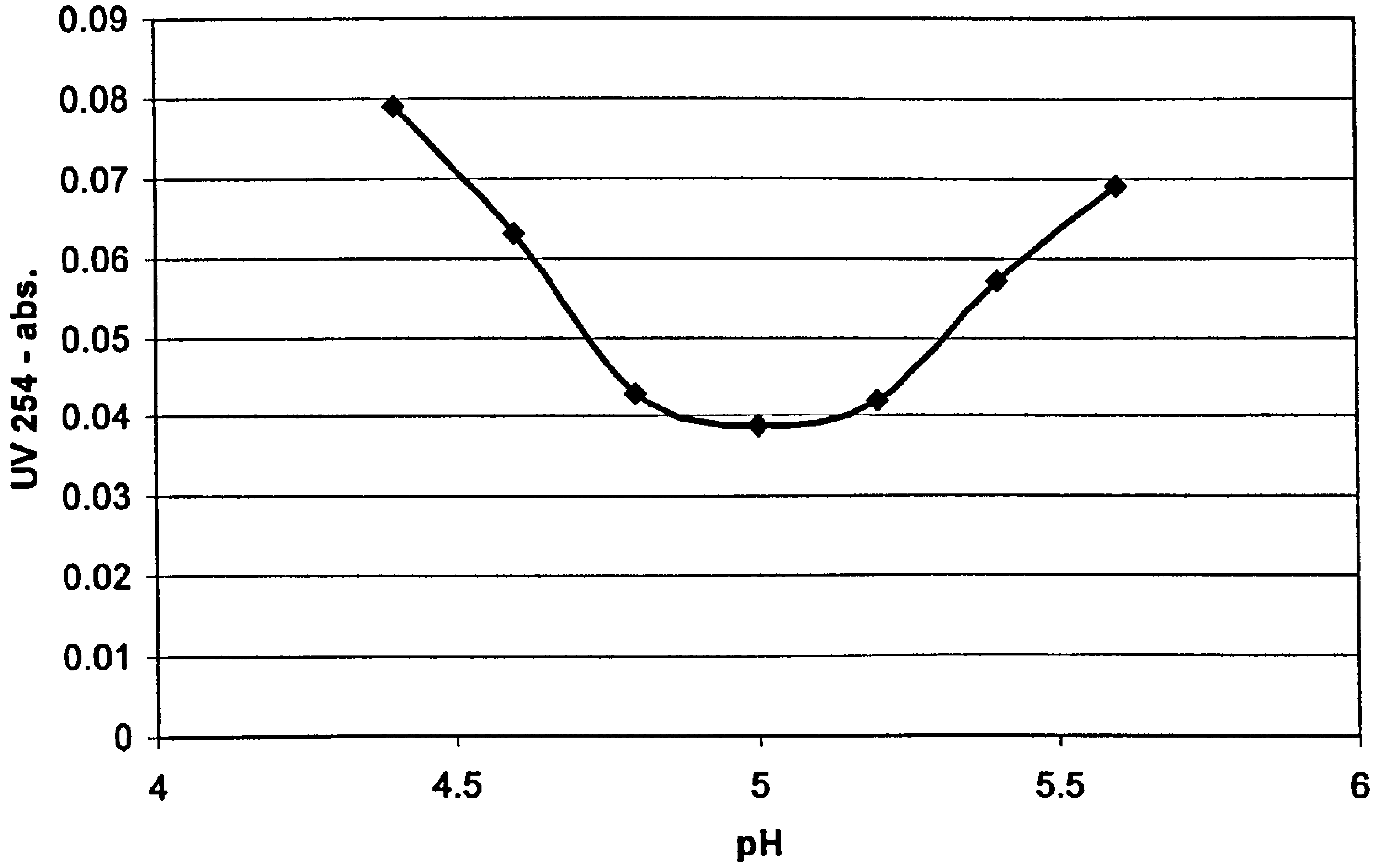

Fig A.2 Impact of pH on ferric chloride coagulation

As both ferric salts have an optimum pH of around 5, addition of hydrochloric acid may be required with low coagulant doses to maintain the pH within an effective range for coagulation. As the addition of HCl raises storage and handling issues in addition to the extra cost involved, water companies may prefer to use alum that has a more alkali pH.

To obtain an optimum pH for alum, a constant coagulant dose of 6 mg/l Al^{3+} was used with varying pH values (**Fig A.3**). The results showed that, for alum, the optimum pH value was ~6.7.

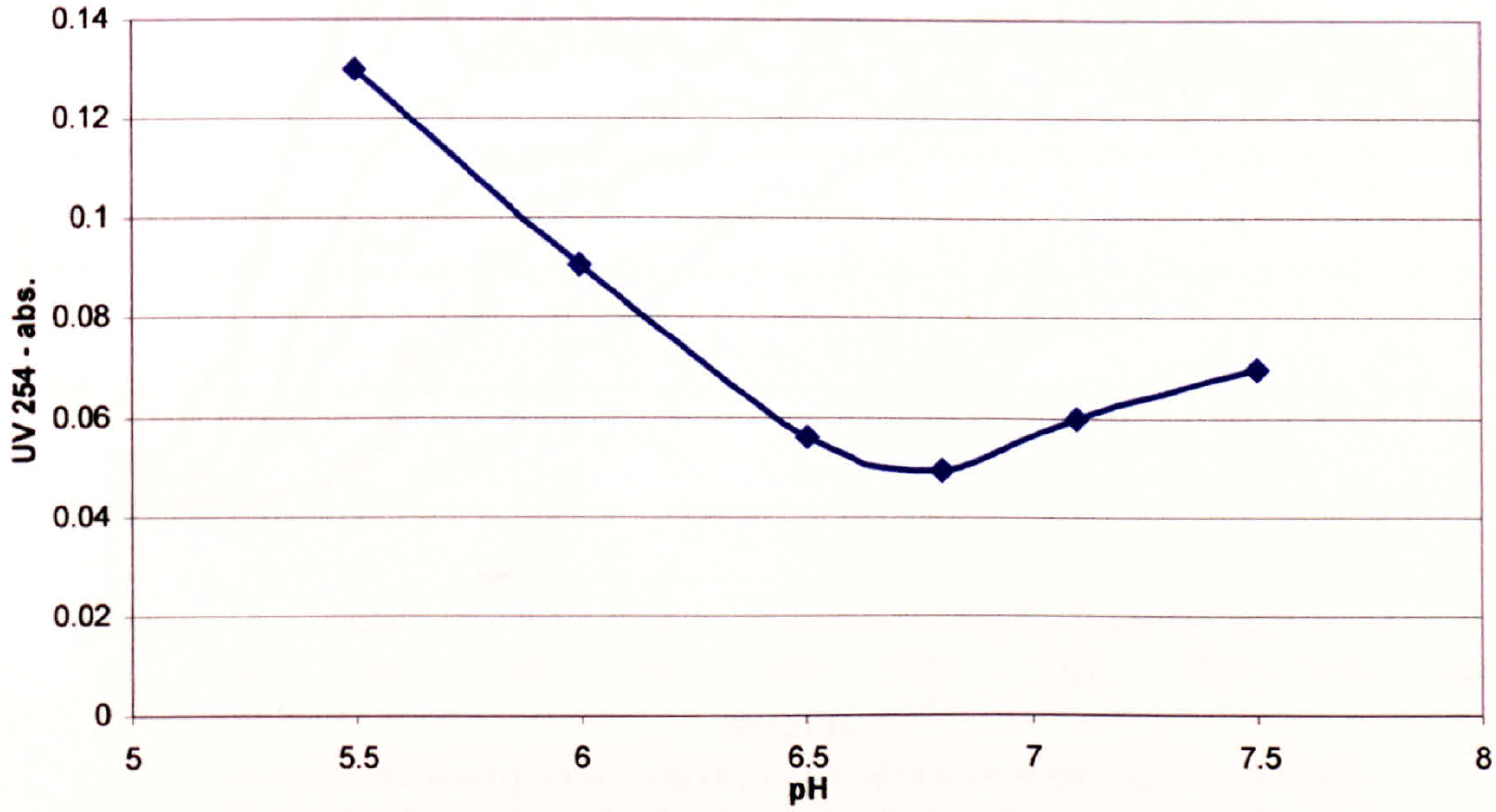

Fig A.3 Impact of pH on alum coagulation

The more alkali nature of alum, although reducing the need for acid addition, has a primary disadvantage in that it is most effective over a more limited pH window of 6.5 to 7.5, whereas ferric salts are known to be more effective over a wider pH window of 4.0 to 11.0. The ferric hydroxide floc is also heavier than the alum floc, improving its settling characteristics. (Ebeling J. M. et al., 2003)

As stated before, the area of interest is in floc growth rather than the settling rates in the coagulation process. Therefore, the PDA was used to investigate the effect of pH on the formation and growth of flocs. **Fig A.4** shows the effect pH has on the floc growth with ferric sulphate.

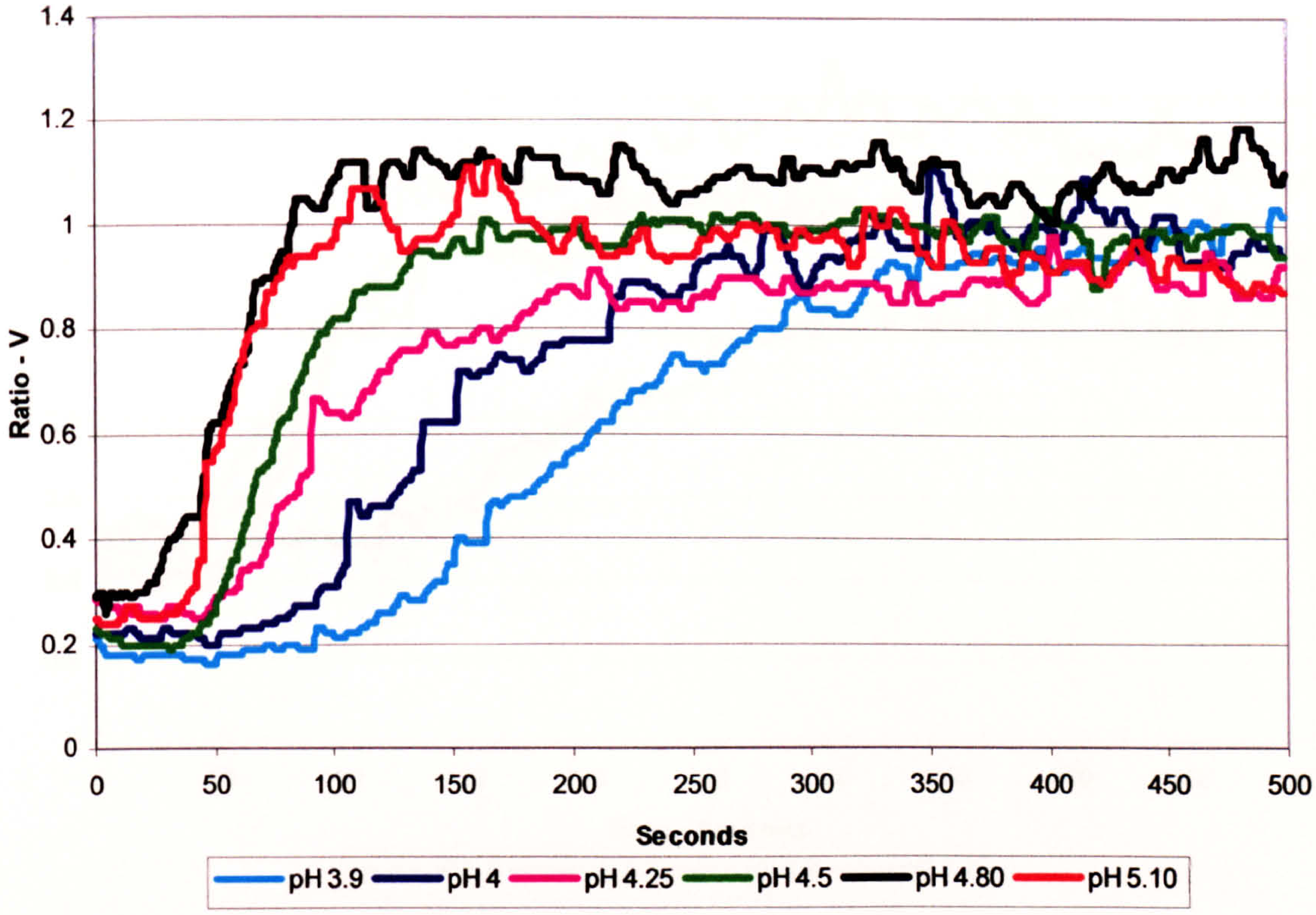

Fig A.4 The effect of pH on the formation of flocs with ferric sulphate

The results of the effect of pH on floc formation showed that by changing the pH from 3.9 through 4.8, the rate of growth increased before decreasing above 4.8. Altering the pH does not have a great effect on the final floc size in this experiment, just on the rate of floc growth. Nevertheless, it should be pointed out that the higher the ratio level the greater the floc size, and as this experiment was conducted at constant shear rate, the pH of 4.8 produced the strongest floc. The fact that flocs were produced even when the pH was 3.9 shows the ability of ferric salts to be used as a coagulant over a wide pH range.

The experiment was repeated with alum as the coagulant, with a coagulant dose of 6 mg/l Al^{3+} (**Fig A.5**). As with the standard jar-test result, the effective pH range for alum is between 6.5 and 7.2. The rate of growth between these pH values is very similar; however, like the ferric sulphate, the optimum pH value also produces the strongest floc, as indicated by the greater ratio value.

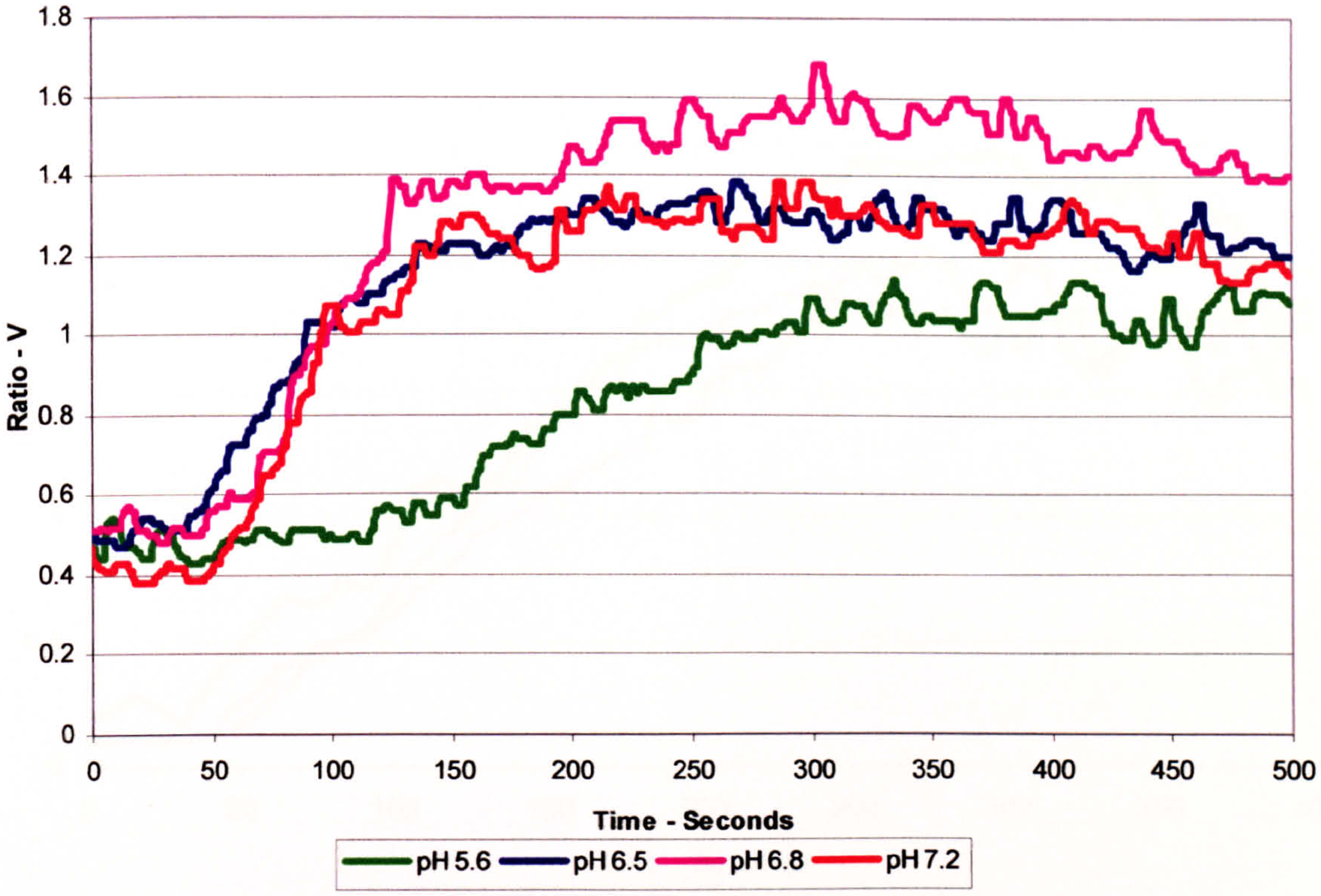

Fig A.5 The effect of pH on alum coagulation

As the above experiments showed the effect pH has on the formation of flocs during rapid mixing, it was important to look at the effect pH has on the growth of flocs during slow mixing. **Fig A.6** shows the growth of ferric sulphate flocs during slow mixing with variable pH.

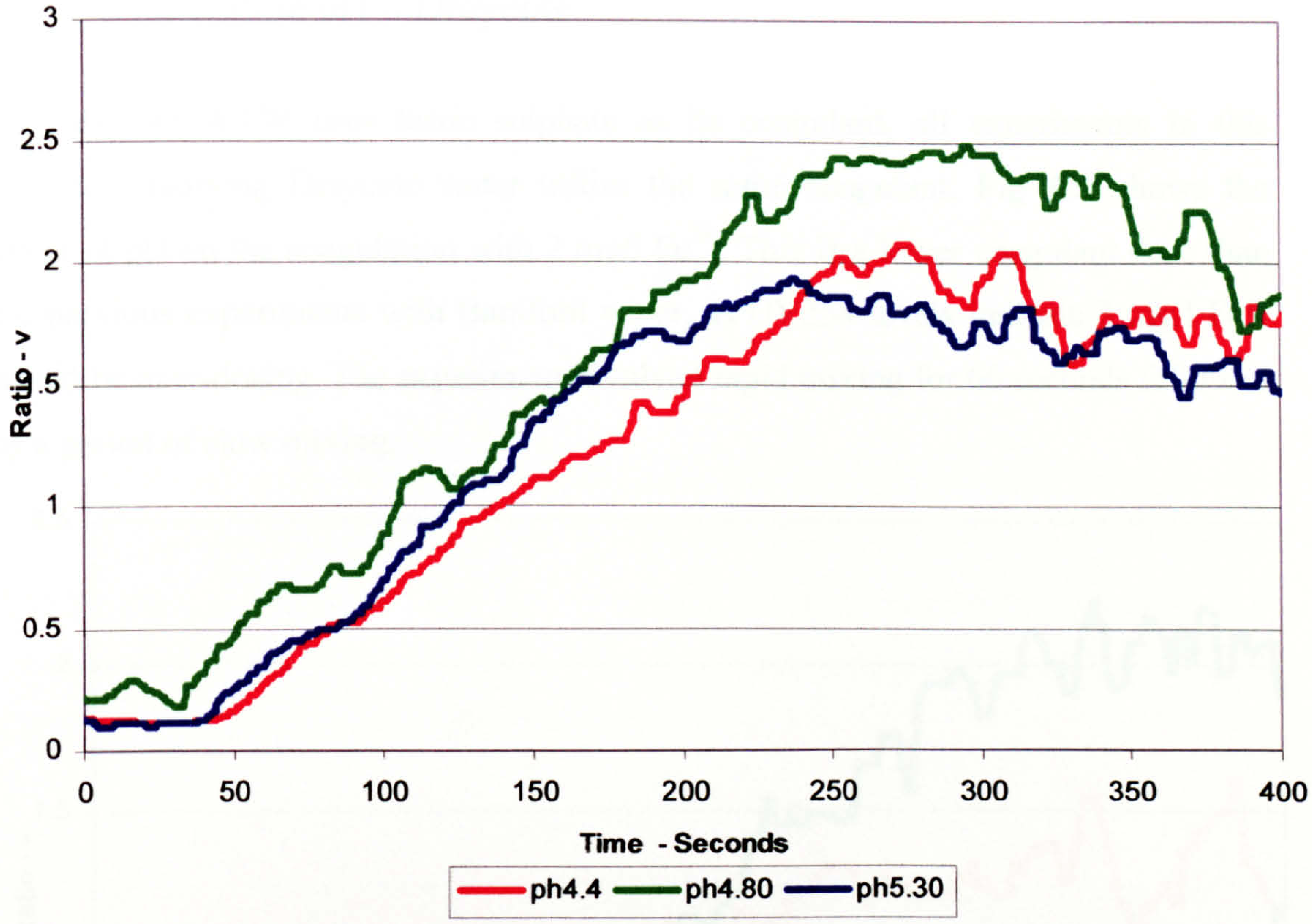

Fig A.6 The effect of pH on coagulation with ferric sulphate

The results shown in **Fig A.6** again highlight the ability of ferric sulphate to coagulate over a wide pH range. Although there is a small difference in the rate of floc growth, the slow mixing regime emphasises that the optimum pH will produce the largest floc, which will settle out more readily than the flocs produced at the lower and higher pH values.

Establishing the correct pH is important, as it affects both the surface charge and character of the organics that are targets for removal by coagulants, as well as the surface charge of the metal hydroxide precipitates that are formed as a consequence of coagulation addition. From a surface chemistry point of view, the optimum pH is the pH value known as the iso-electric point, at which the overall floc charge is zero.

The results shown represent the effect pH has on the growth of flocs with Bamford water. As the research will also investigate the use of coagulation and UF membranes to treat lowland water, it was important to investigate the coagulation pH of Draycote water

A.3.2 Coagulation pH – Draycote

As Draycote WTW uses ferric sulphate as its coagulant, all experiments in this research involving Draycote water utilise the same coagulant. **Fig A.7** shows the effect of pH on the coagulation with 2 mg/l Fe^{3+}. This is a lower coagulant dose than the previous experiments with Bamford water, as UV254 levels indicate 3 mg/l Fe^{3+} would be over-dosing. The experiment involved rapid mixing for 60 seconds followed by a period of slow mixing.

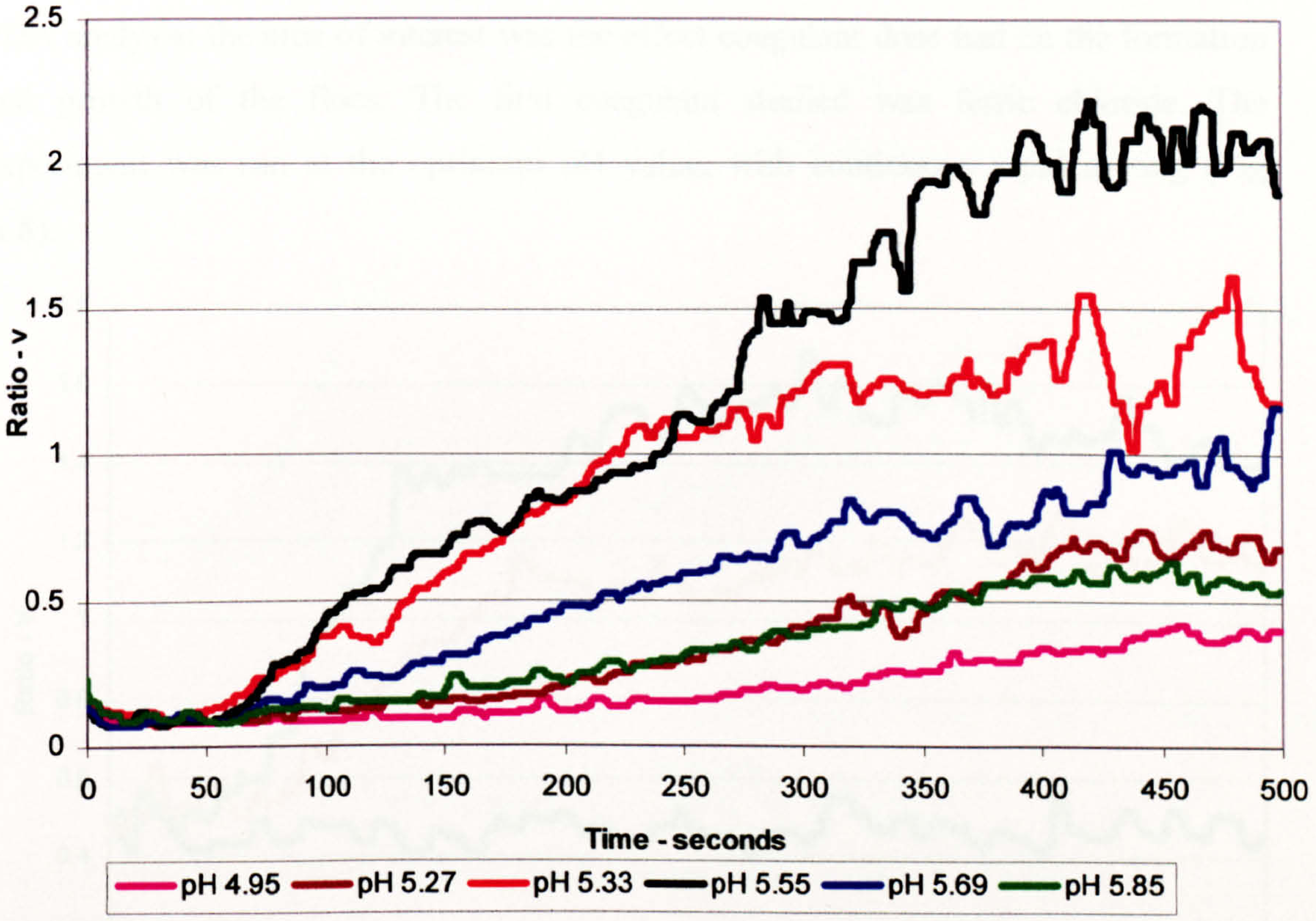

Fig A.7 The effect of pH on ferric sulphate coagulation of Draycote water

The results show that the pH of coagulation greatly affects the growth of flocs; although flocs are produced over the range of pH values, there is a significant improvement in performance at the optimum pH of 5.55. This is significantly higher than the pH of coagulation of Bamford water. This may be due to the differences in the charged organic species present in each of the waters.

A.3.3 Coagulant dose – Bamford

The key process controls for coagulation are coagulant dose and pH control. Even when a pH-adjusting chemical (e.g. Lime) is not used, the addition of the coagulant changes the pH, and this affects the coagulation process. It is important therefore to investigate the role of coagulant dose in the coagulation process.

To determine the amount of coagulant required, standard jar-tests were replaced with PDA analysis: the area of interest was the effect coagulant dose had on the formation and growth of the flocs. The first coagulant studied was ferric chloride. The experiment was run at the optimum pH value, with continuous rapid mixing (**Fig A.8**).

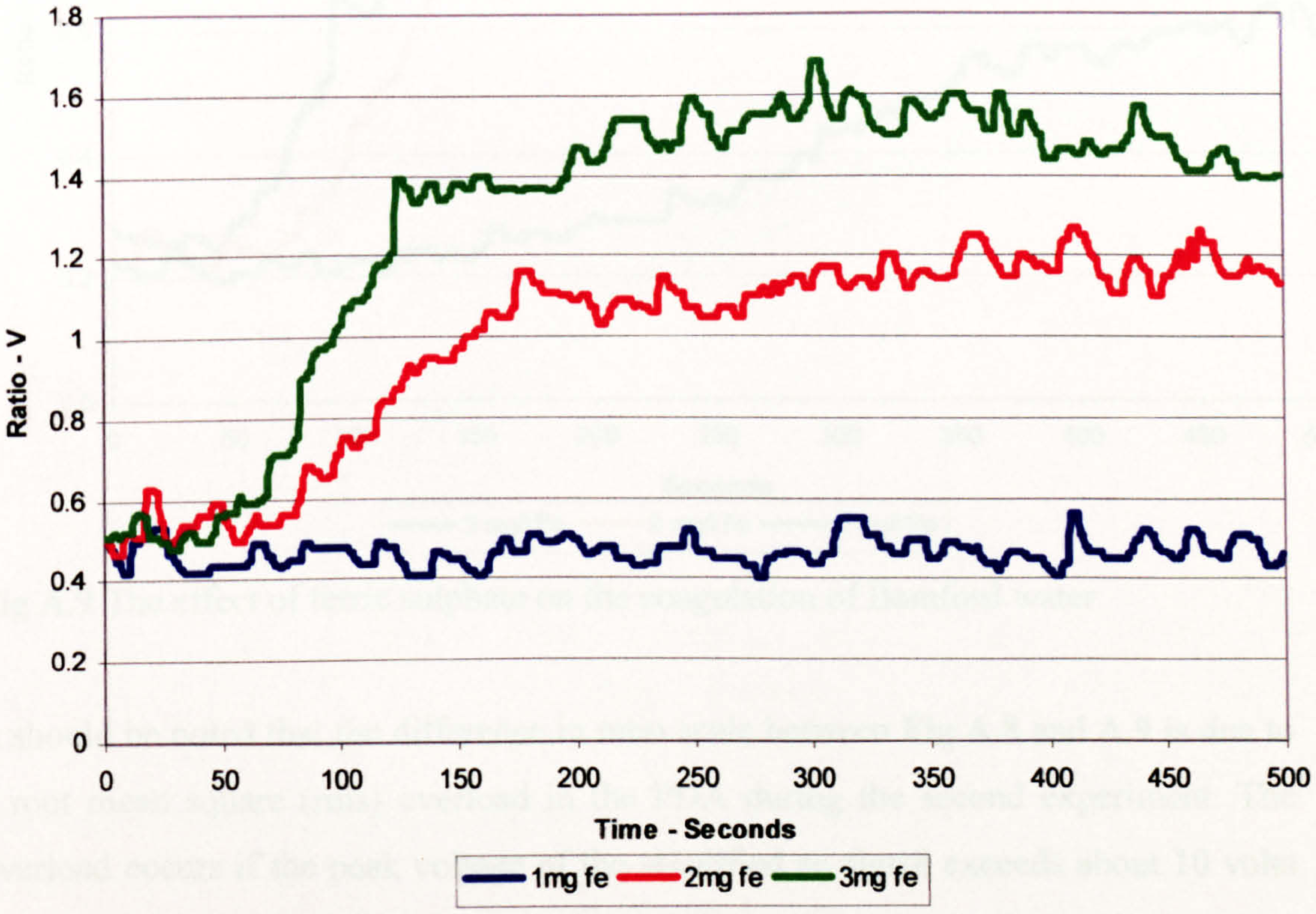

Fig A.8 The effect of ferric chloride on coagulation of Bamford water

The result shows that, at the optimum pH, the amount of coagulant available greatly affects the coagulation performance. At 1 mg/l Fe^{3+}, there were not many flocs produced indicating insufficient coagulant. The amount of flocs produced increased with coagulant dose, 3 mg/l Fe^{3+} performing better than 2 mg/l Fe^{3+}. The rate of floc growth was greater at the higher dose, but more significant was the size of floc that the higher dose achieved. The higher dose produced a stronger, more stable floc, as indicated by the higher ratio value.

As a comparison of coagulation performance, the experiment was repeated with ferric sulphate. The optimum pH was 4.8, as indicated by the ferric sulphate pH experiments.

The amount of coagulant varied from 1 to 3 mg/l Fe^{3+} (**Fig A.9**).

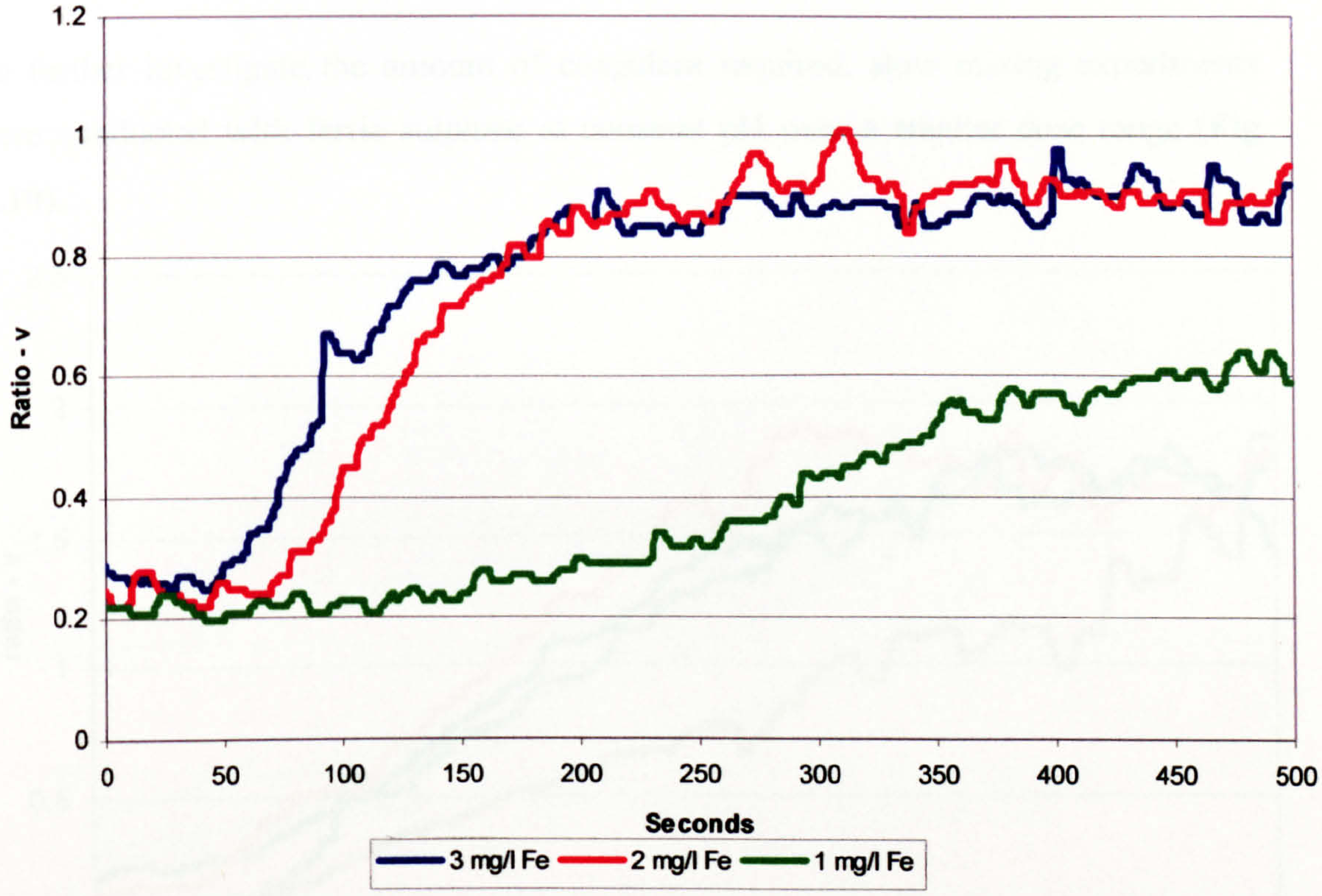

Fig A.9 The effect of ferric sulphate on the coagulation of Bamford water

It should be noted that the difference in ratio scale between **Fig A.8** and **A.9** is due to a root mean square (rms) overload in the PDA during the second experiment. The overload occurs if the peak voltage of the amplified ac signal exceeds about 10 volts or the rms value is greater than about 6 volts. The problem was corrected by reducing the setting on the rms gain. The rms gain is a ten turn precision potentiometer that allows adjustment of the main ac amplifier between 5 and 500. The difference in ratio values allows qualitative but not quantitative analysis between the two ferric coagulants.

The results (fig A.9) show that the amount of ferric strongly affects the creation of the flocs. The amount of ferric hydroxide available dictates the rate of growth. A dose of 3 mg/l Fe^{3+} has the quickest growth rate. 2 mg/l Fe^{3+}, although slightly slower does achieve the same level of floc formation. 1 mg/l Fe^{3+} of ferric sulphate, unlike the case with ferric chloride, does form flocs, albeit very slowly. The fact that 2 mg/l Fe^{3+} reaches practically the same level of floc growth as 3 mg/l Fe^{3+} indicates excess coagulant with 3 mg/l Fe^{3+}.

To further investigate the amount of coagulant required, slow mixing experiments were conducted with ferric sulphate at constant pH over a smaller dose range (**Fig A.10**).

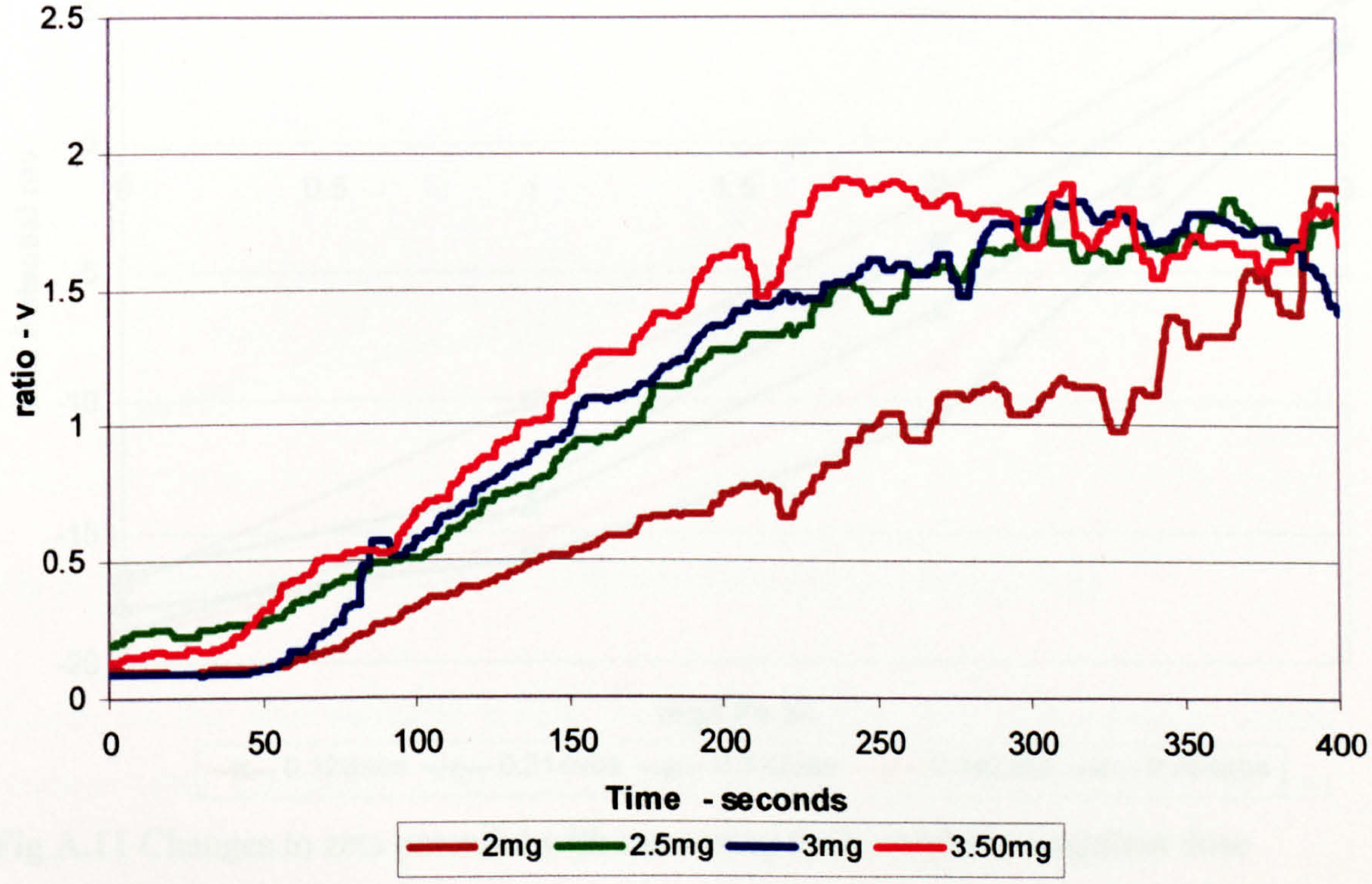

Fig A.10 The effect of ferric sulphate dose on flocculation

The results show that although the dose of 3.5 mg/l Fe^{3+} has the greatest growth rate, the similarities between 3 and 2.5 mg/l Fe^{3+} indicate that the performance at the higher dose represents overdosing. The slight improvement in floc growth obtained at the higher dose is not significant enough to merit the costs associated with the increased amount of coagulant.

To further explain the results, zeta potential measurements were taken for the raw water and for the coagulated samples at different coagulant dosage (**Fig A.11**). As the raw water quality changes throughout the year, zeta potential experiments were conducted with water containing various amounts of organic material, as indicated by UV254 abs. levels.

The raw water used in the ferric sulphate experiment (**Fig A.11**) with slow mixing is indicated in **Fig.A.10** as having an UV254 abs. reading of 0.442.

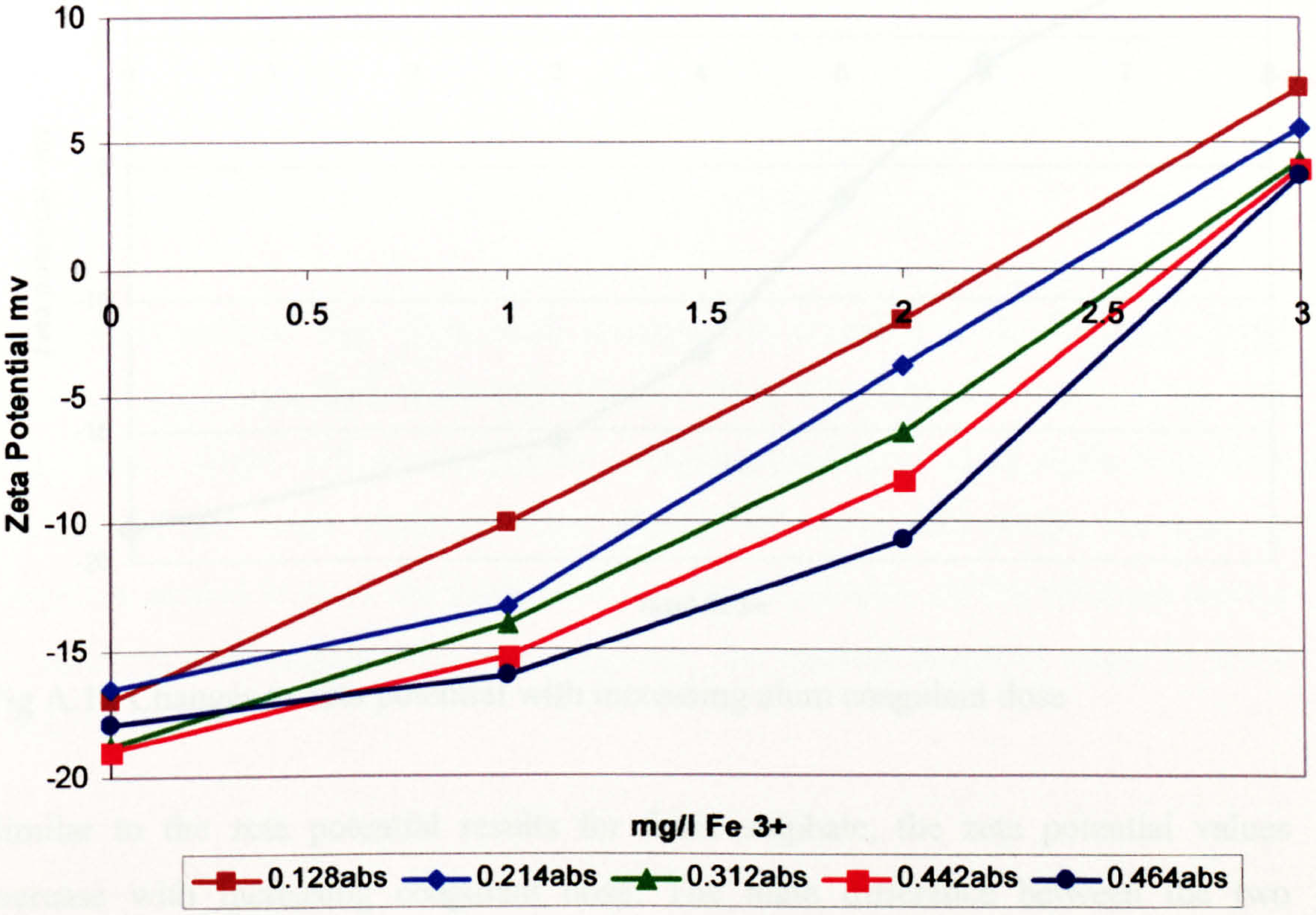

Fig A.11 Changes to zeta potential with increasing ferric sulphate coagulant dose

The results show that the zeta potential of the raw water is negative (>-15mv), but increases in value with the addition of positive ferric hydroxide colloids. As nearly all colloidal impurities in water are negatively charged, and hence stabilized by electrical repulsion forces, the addition of positively charged hydrolysis products reduces the zeta potential of the colloidal matter towards zero, eliminating the electrical repulsion between the colloidal particles and promoting greater floc growth.

As the optimum coagulant dose is generally associated with a near zero zeta potential, the results for Bamford water show that the optimum ferric sulphate dose, lies between 2.2 and 2.8 mg/l Fe^{3+}, the value being dependant on the water quality.

The changes in zeta potential due to varying alum coagulant dose were also investigated (**Fig A.12**). The pH of the experiment was kept constant, so that changes in zeta potential were due to coagulant addition rather than pH.

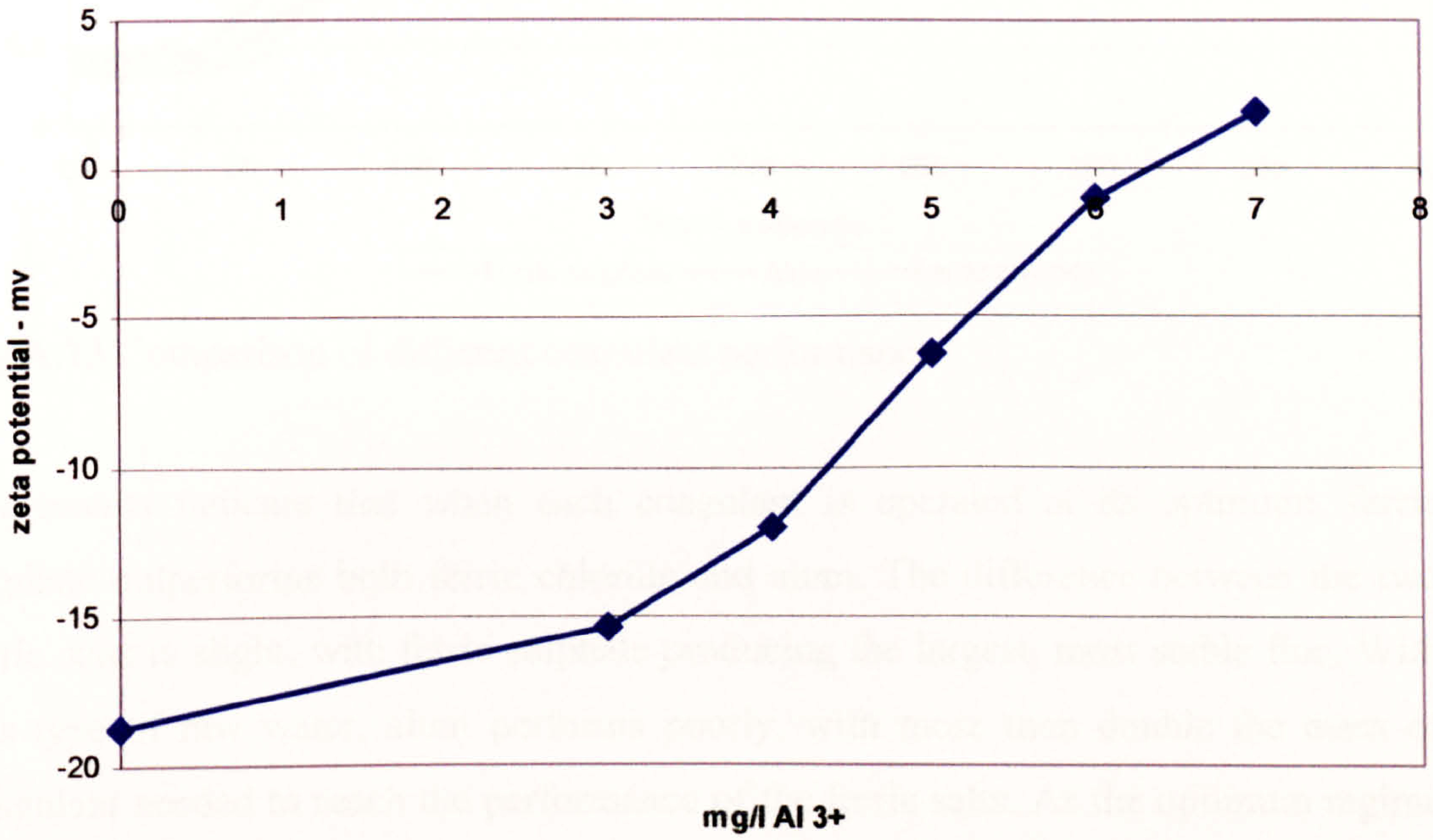

Fig A.12 Changes to zeta potential with increasing alum coagulant dose

Similar to the zeta potential results for ferric sulphate, the zeta potential values increase with increasing coagulant dose. The main difference between the two coagulants is the amount of alum required to reach the iso-electric point.

For a direct comparison between the performance of alum, ferric chloride and ferric sulphate in treating Bamford water, an experiment was conducted whereby each coagulant was added at its optimum pH and dose (**Fig A.13**).

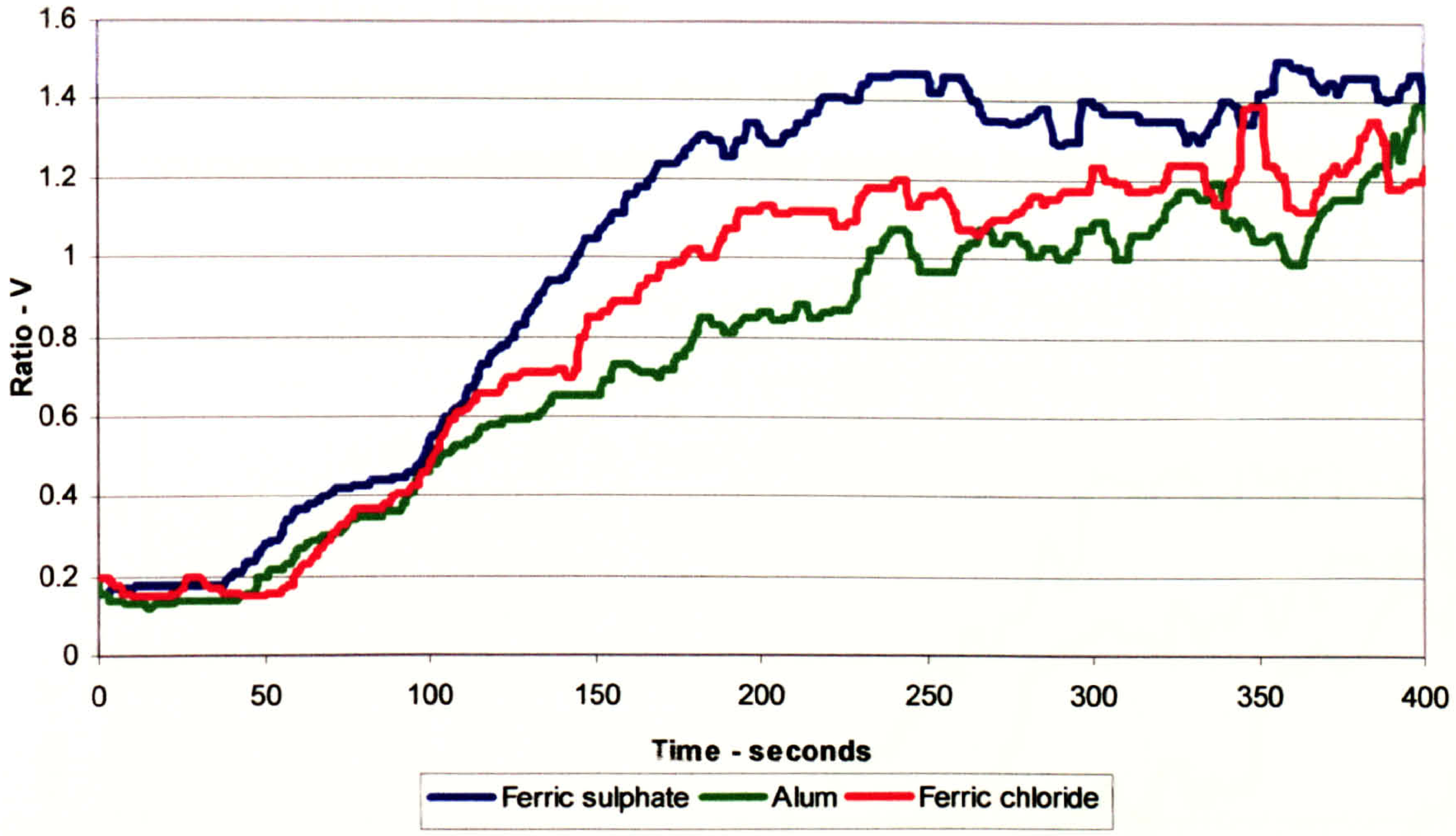

Fig A.13 Comparison of different coagulant performance

The results indicate that when each coagulant is operated at its optimum, ferric sulphate outperforms both ferric chloride and alum. The difference between the two ferric salts is slight, with ferric sulphate producing the largest, most stable floc. With this type of raw water, alum performs poorly, with more than double the mass of coagulant needed to reach the performance of the ferric salts. As the optimum regime is based on performance, the best coagulant for treating Bamford water is ferric sulphate.

A.3.4 Coagulant dose - Draycote

To determine the optimum coagulant dose with ferric sulphate to treat Draycote water, experiments were conducted with varying coagulant levels at a pH of 5.5 (**Fig A.14**).

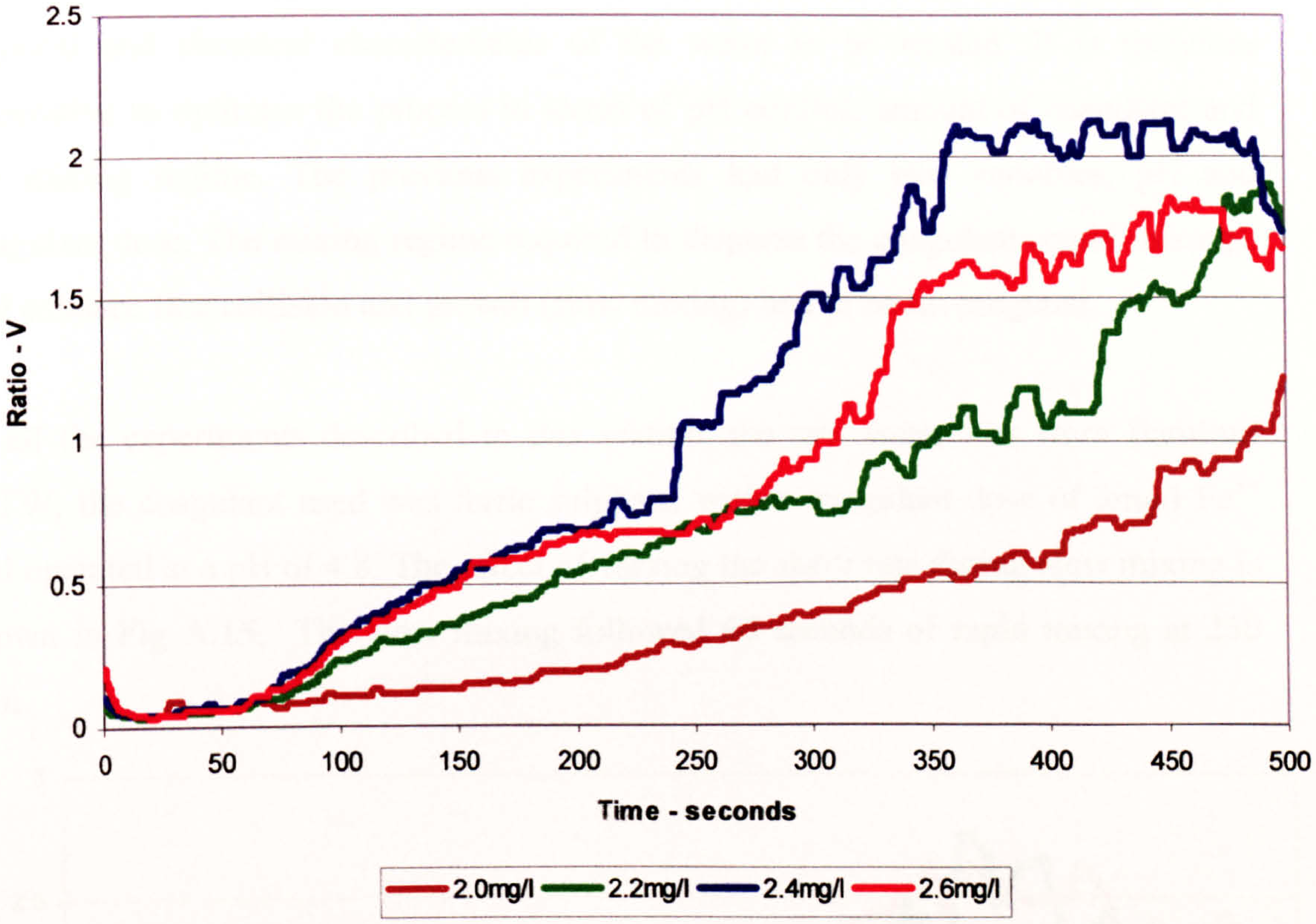

Fig A.14 The effect of ferric sulphate dose on flocculation of Draycote water

The optimum coagulant dose is usually determined by the UV254 value, in this case 0.115 abs., which would lead to a dose of 2 mg/l Fe^{3+}, as determined by the UV254/coagulant dose calibration curve. However the optimum coagulant dose as indicated by the PDA results is 2.4 mg/l Fe^{3+}. This discrepancy is due to the fact that Draycote water contains a high percentage of non-absorbing organics, requiring a greater amount of coagulant that that indicated by UV254 readings.

A.3.5 Optimisation of the mixing regime

The efficiency of coagulation for the removal of NOM is variable, depending on the physical and chemical characteristics of the water to be treated. It is therefore imperative to optimise the process in terms of pH control, amount of coagulant and the mixing regime. The previous experiments had only two variables, pH and coagulant dose. The mixing regime required to disperse the coagulant (rapid mixing), and enhance floc collision and growth (slow mixing) had to be investigated.

In all the experiments described in this section, the raw water was from Bamford WTW; the coagulant used was ferric sulphate, with a coagulant dose of 3mg/l Fe^{3+} and operated at a pH of 4.8. The effect of varying the shear rate during slow mixing is shown in **Fig A.15**. The slow mixing followed 60 seconds of rapid mixing at 250 rpm.

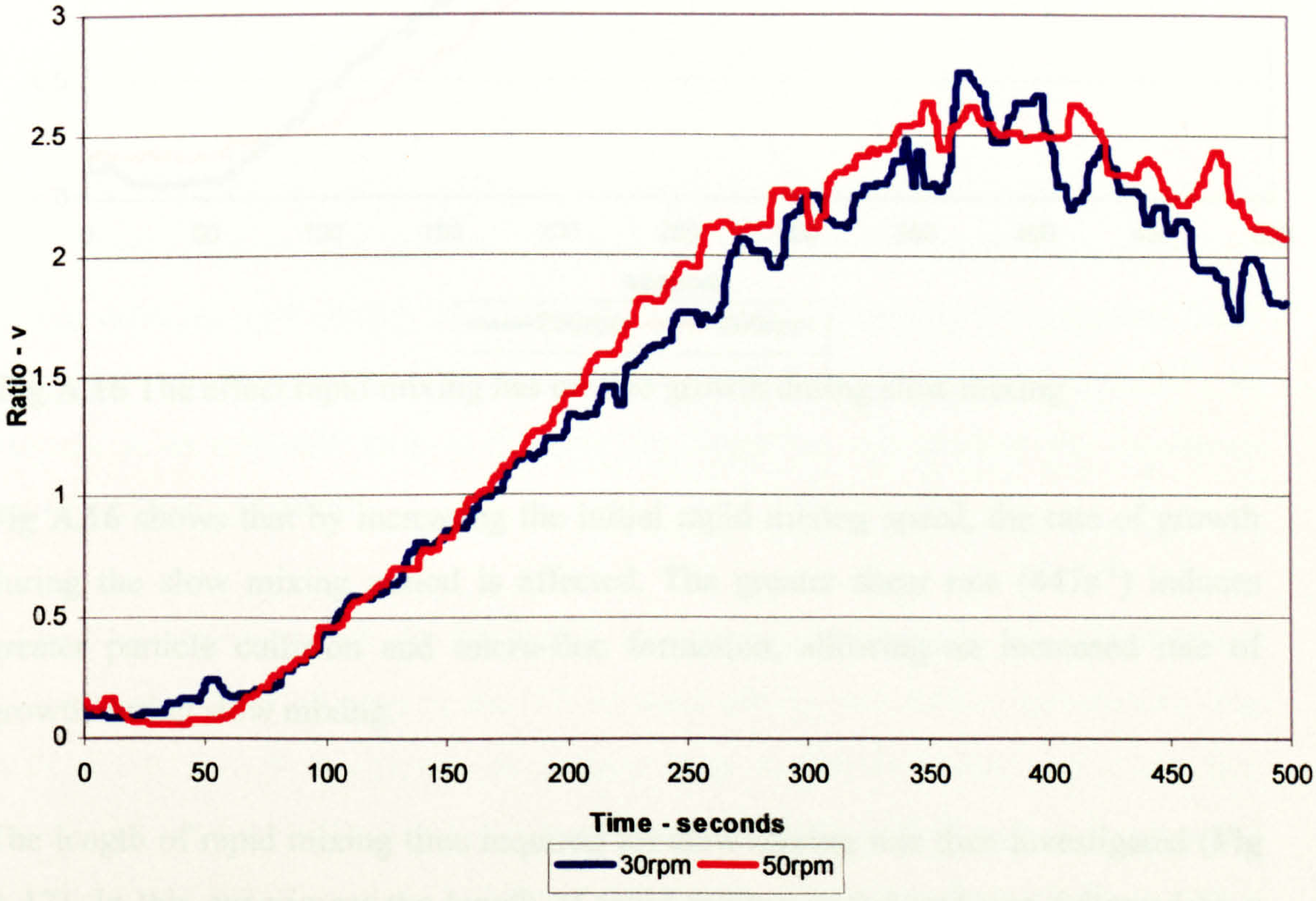

Fig A.15 The effect of slow mixing on the growth of flocs

Both slow mix parameters show similar rates of growth, with 50 rpm being slightly quicker. The final floc size is less than at 30 rpm due to floc break-up at the greater shear rate. The differences between the two speeds are effectively negligible, and as such all experiments involving slow mixing have an rpm setting of 30 ($G = 19\ s^{-1}$).

To investigate the role of rapid mixing and floc formation on floc growth, an experiment was conducted with different rapid mix speeds followed by slow mixing. 60 seconds of rapid mixing, at different rpm speeds, was followed by slow mixing at 30 rpm (**Fig A.16**).

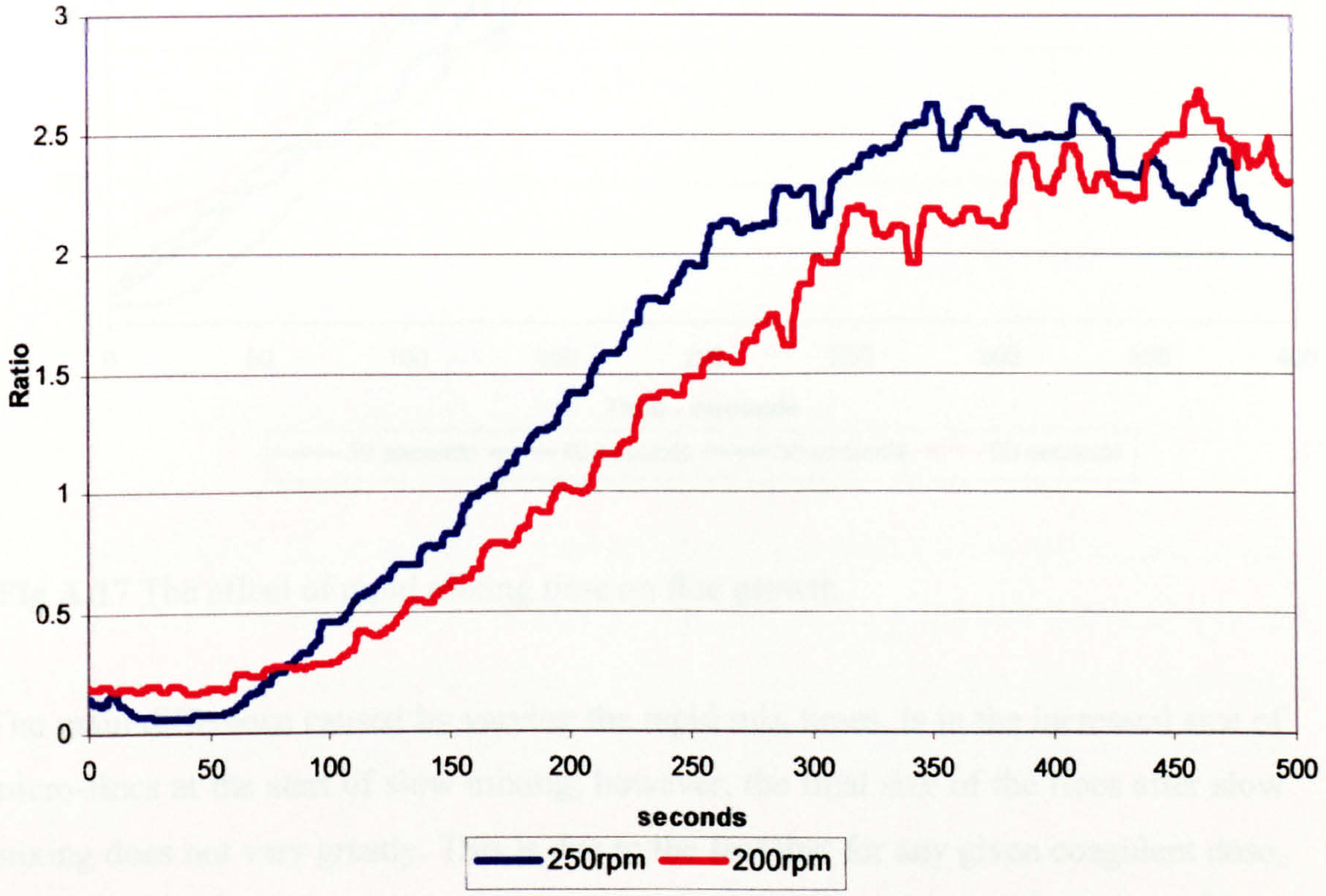

Fig A.16 The effect rapid mixing has on floc growth during slow mixing

Fig A.16 shows that by increasing the initial rapid mixing speed, the rate of growth during the slow mixing period is affected. The greater shear rate ($447s^{-1}$) induces greater particle collision and micro-floc formation, allowing an increased rate of growth during slow mixing.

The length of rapid mixing time required for slow mixing was then investigated (**Fig A.17**). In this experiment the length of rapid mixing varied and was followed by a period of slow mixing. The graph only shows the slow mixing response to the rapid mixing times.

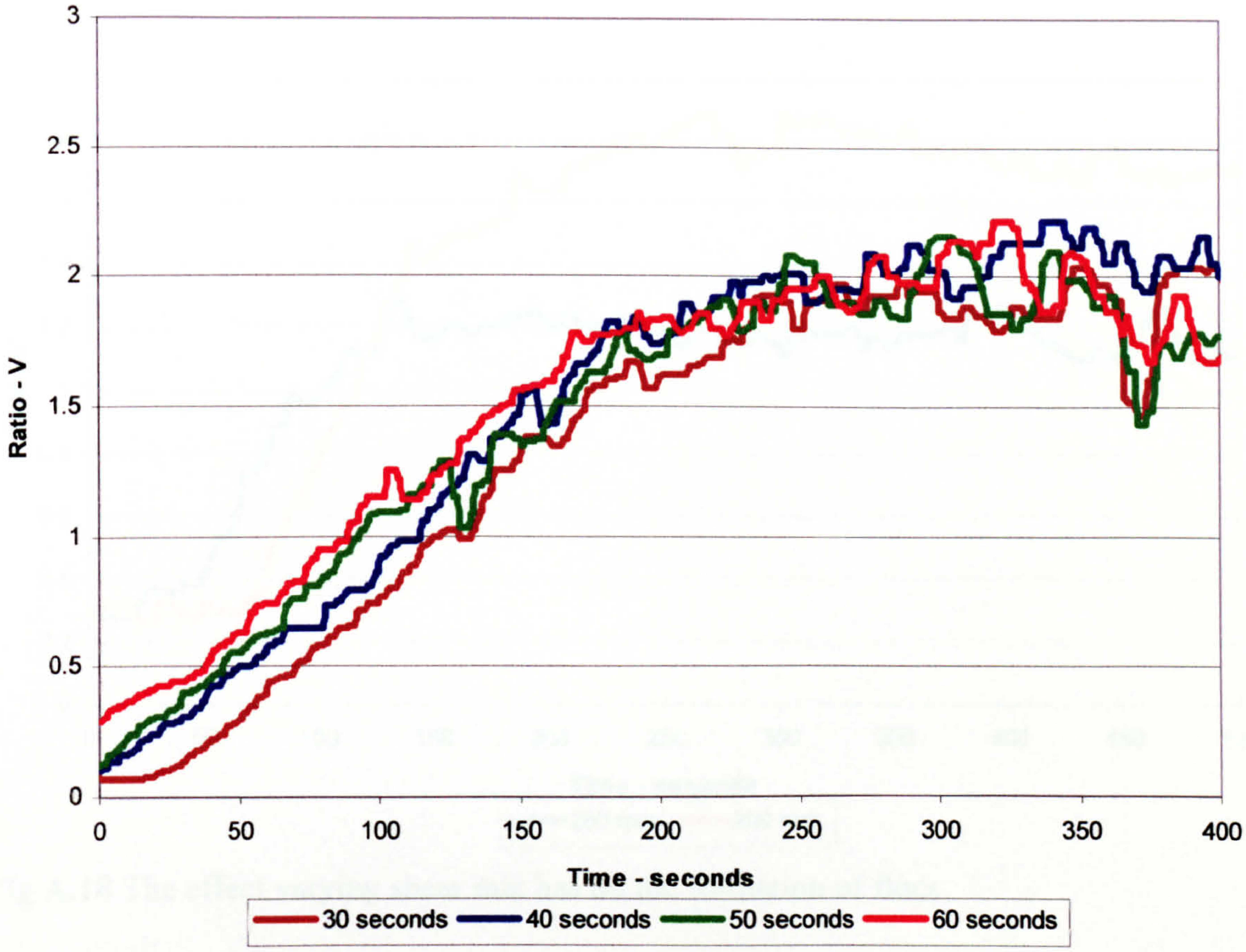

Fig A.17 The effect of rapid mixing time on floc growth

The main difference caused by varying the rapid mix times, is in the increased size of micro-flocs at the start of slow mixing; however, the final size of the flocs after slow mixing does not vary greatly. This is due to the fact that for any given coagulant dose, an approx. constant number of flocs produced. In this experiment with 3 mg/l Fe^{3+}, 30 seconds is an adequate time to disperse the coagulant and produce the maximum number of flocs possible.

Since this current work is interested in removing the flocs by ultrafiltration membranes and not by settling, the role of rapid mixing was further investigated. **Fig A.18** shows the effect different shear rates have on floc formation and initial floc growth during the rapid mixing phase. In this experiment with 3 mg/l Fe^{3+}, the rapid mixing period was extended to 480 seconds to investigate the effect of shear on floc strength.

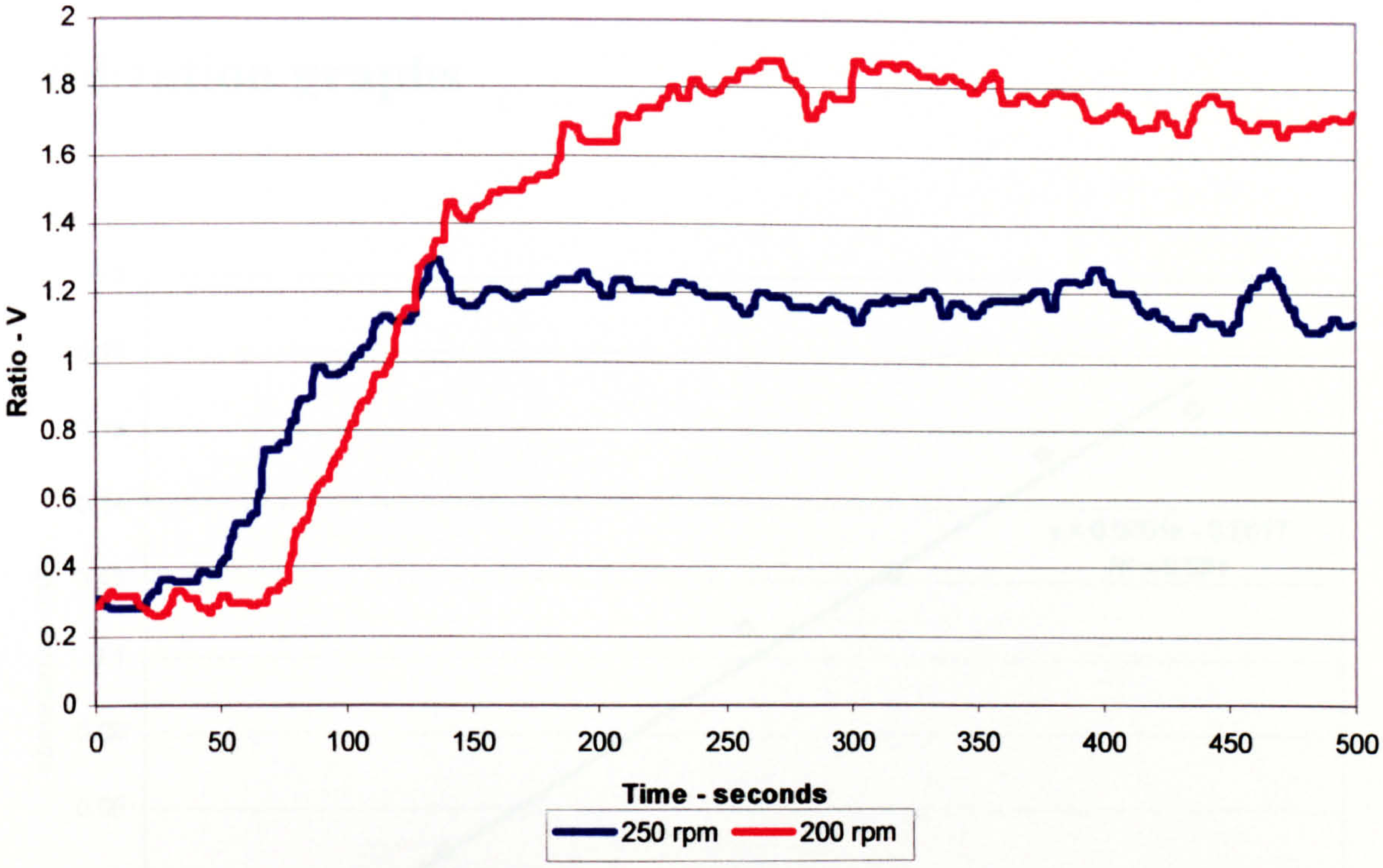

Fig A.18 The effect varying shear rate has on the formation of flocs

The faster rpm produces the greater rate of growth, the higher shear rate increases the pin floc formation through greater dispersion of coagulant. However the final size of the flocs at 250 rpm is less than that at 200rpm; this is due to the greater shear rate (447 s^{-1} compared to $321s^{-1}$) limiting the floc growth, due to shear induced floc breakage.

The PDA, although able to accurately show the rate of growth of the flocs, can only provide a guideline as to floc size. The previous experiment showed that flocs form with a mixing rate of 250rpm. But is rapid mixing alone sufficient to remove all the natural organic matter from the water?

A discussion on the results presented here as well as the removal of NOM during the mixing process and the role of excess iron is discussed in full in **Chapter 6 Optimisation of the coagulation process**.

Appendix B

Calibration graphs

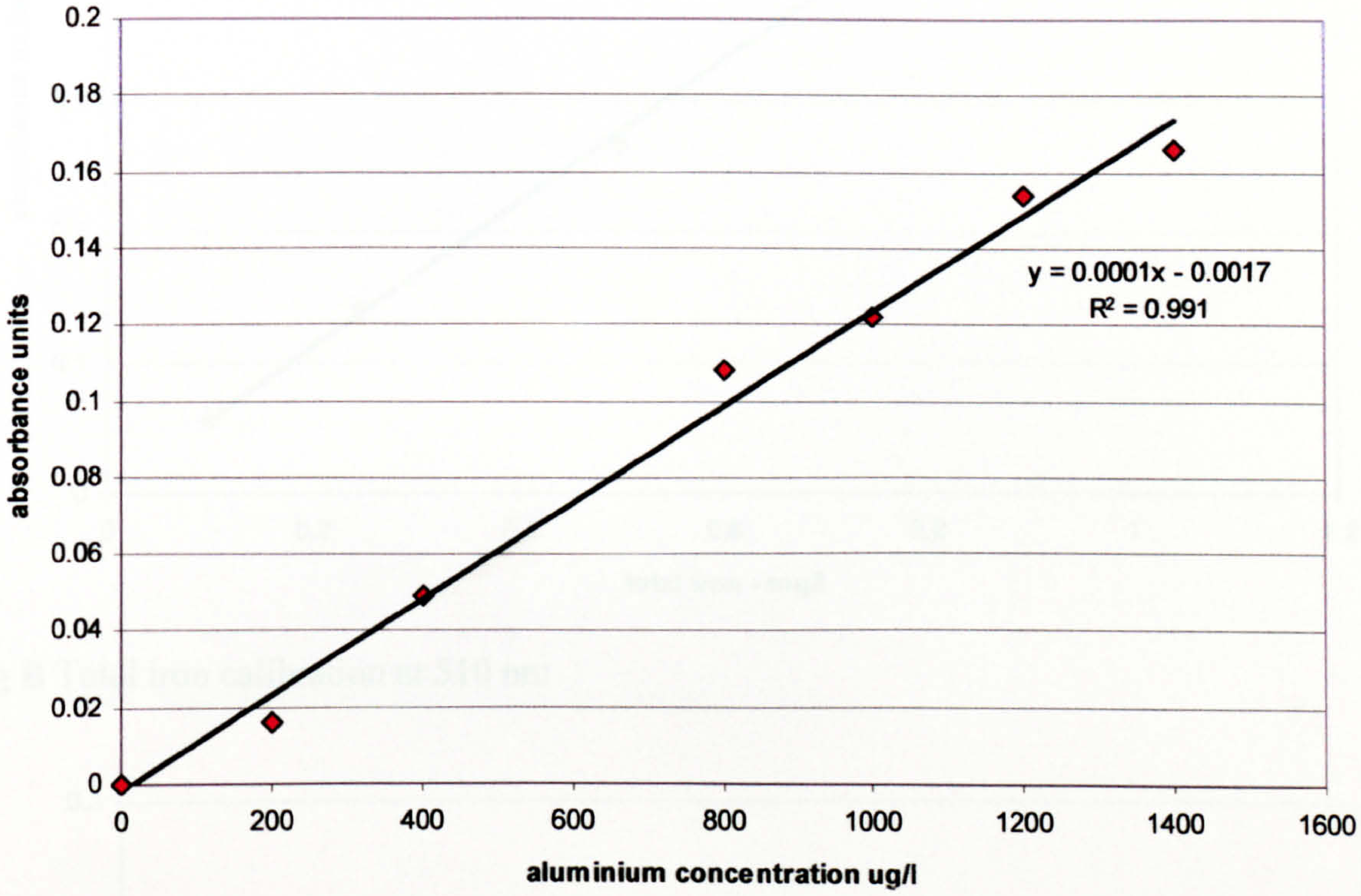

Fig A Aluminium calibration at 535 nm

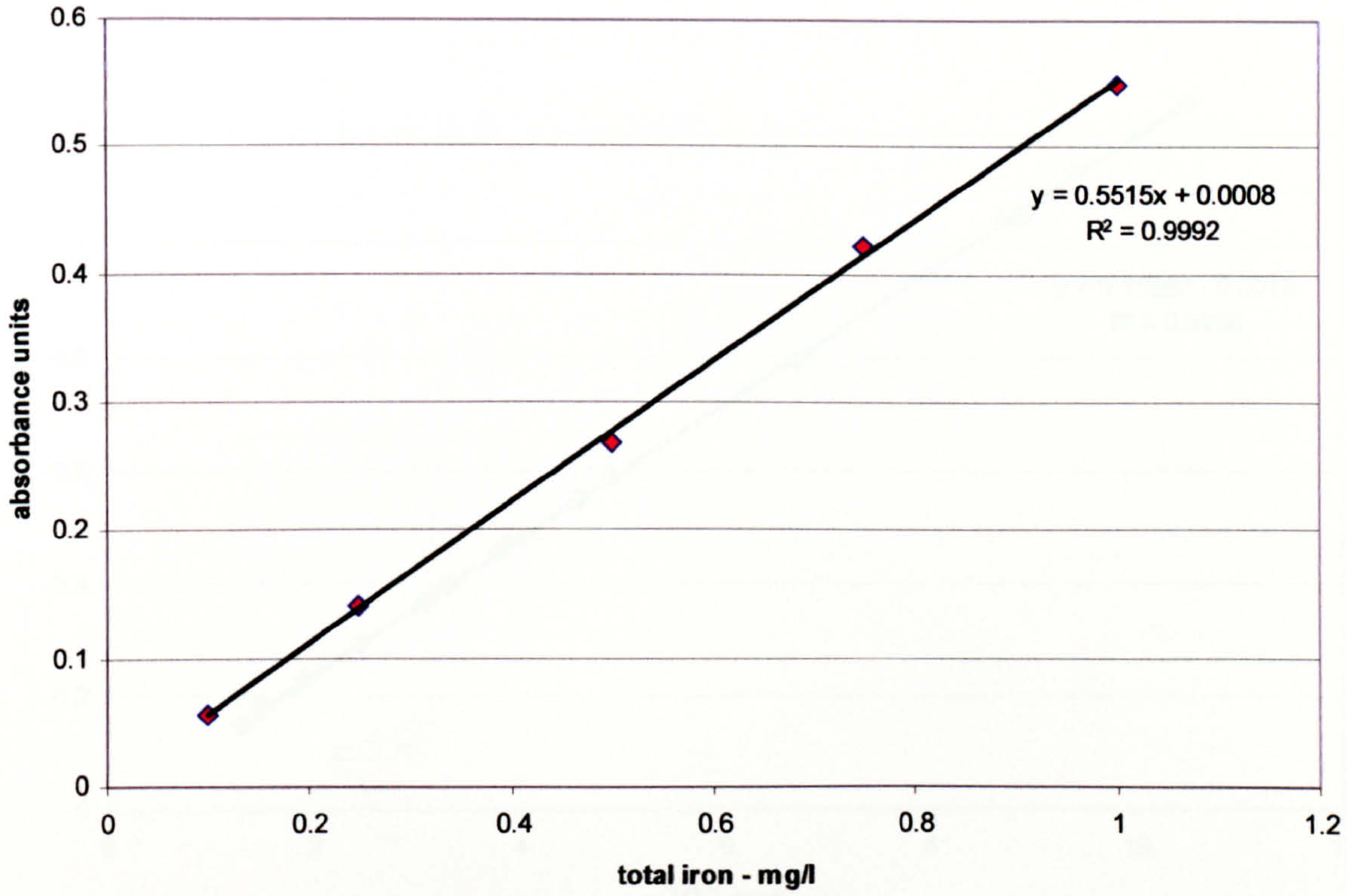

Fig B Total iron calibration at 510 nm

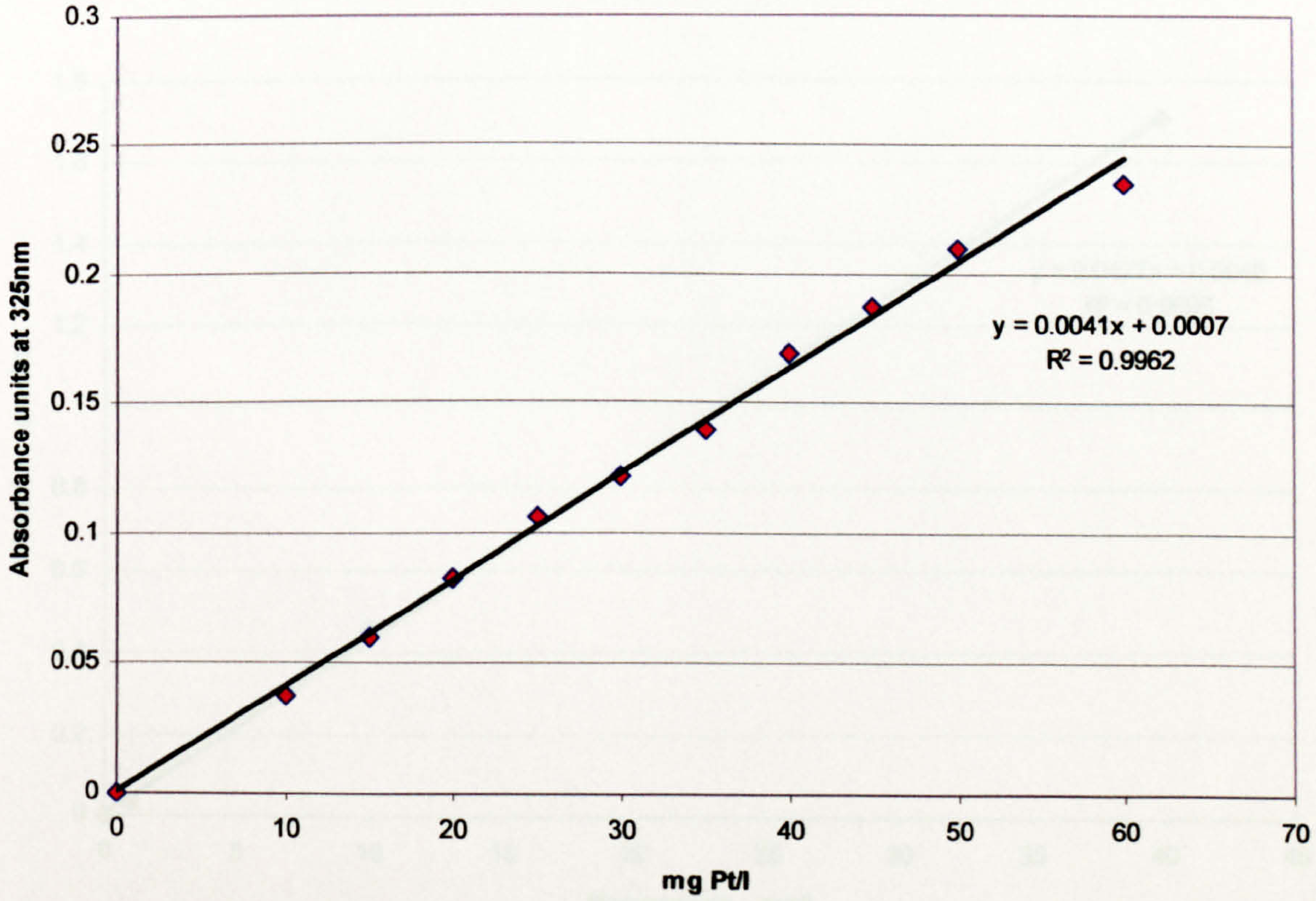

Fig C Colour calibration at 325 nm

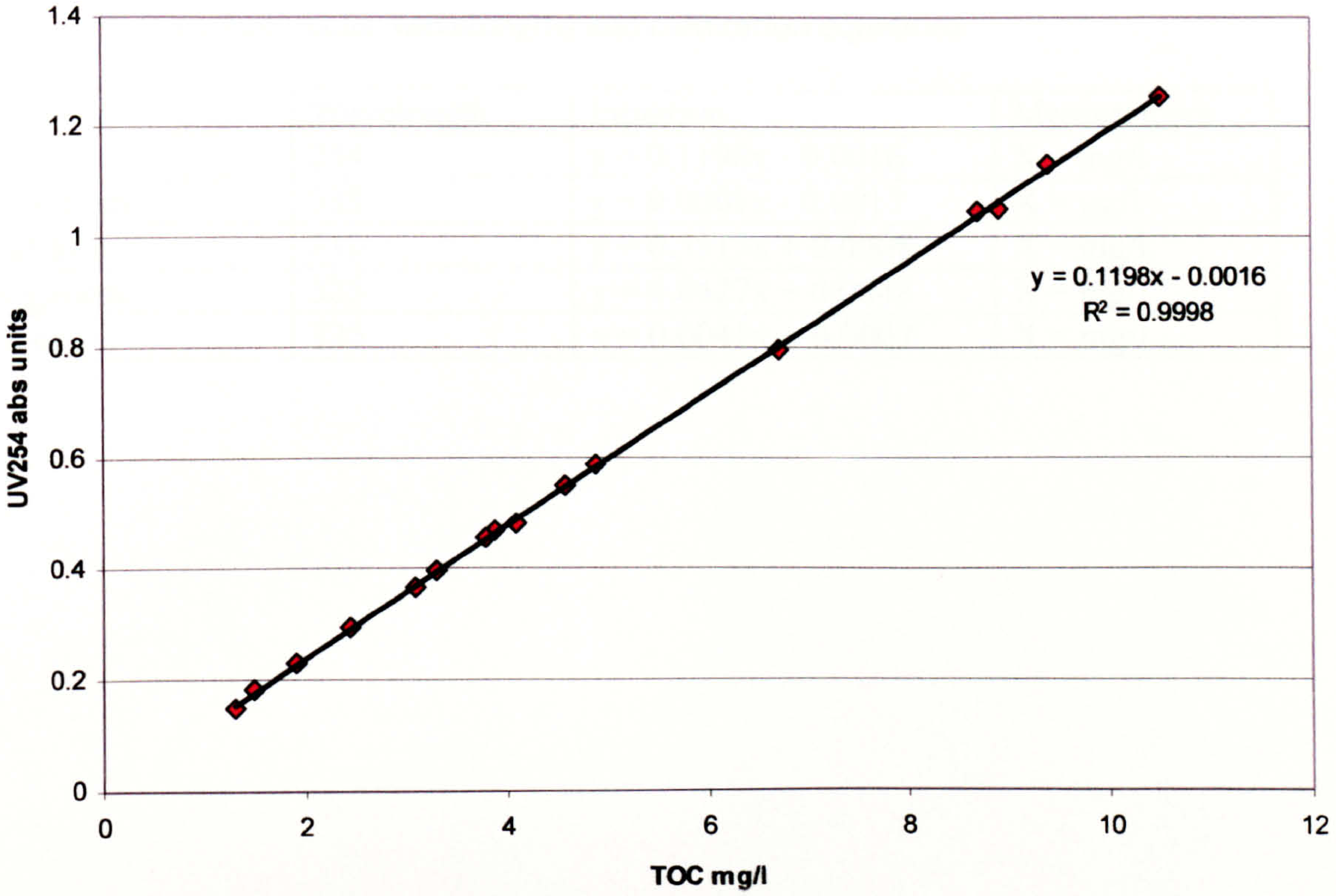

Fig D Total organic carbon calibration at 254 nm

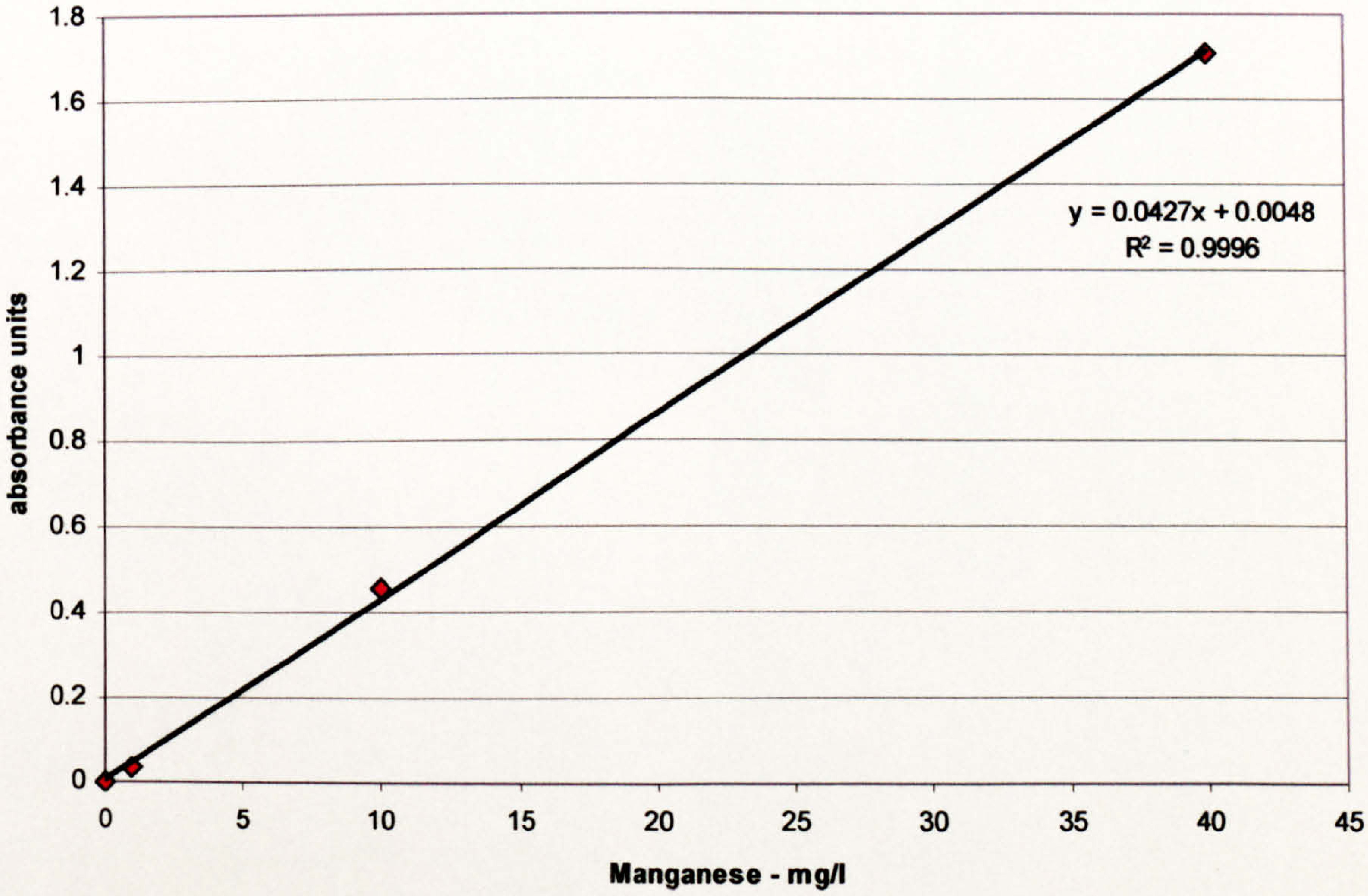

Fig E Manganese calibration at 525 nm

Table A Spectrophotometer wavelengths and calibration equations

Parameter	Wavelength	Equation	Measurement
UV254	254	$y = 0.1198x - 0.0016$	X = mg/l
Aluminium	535	$y = 0.0001x - 0.0017$	X = µg/l
Total Iron	510	$y = 0.5515x + 0.0008$	X = mg/l
Manganese	525	$y = 0.0427x + 0.0048$	X = mg/l
Colour	325	$y = 0.0041x + 0.0007$	X = mg/l

Appendix C - UK membrane municipal plant

Location	Type	Capacity m^3/d	Client	Membrane supplier	Date	*Status*
Potable						
Achnasheen	NF	50	NoSWA	PCI	2001	Operational
Alderley	UF	5,000	Bristol W	Kalsep	2001	Operational
Allenheads	UF	130	NWL	Kalsep	2000	Operational
Ardeonaig	NF	100	ESWA	PCI	2002	Commiss.
Ardfern	NF	110	WoSWA	PCI	2000	Operational
Arinagour	NF	42	WoSWA	PCI	1999	Operational
Backies	NF	2,200	NoSWA	Koch/FS	1999	Operational
Badachro	NF	200	NoSWA	Koch/FS	2000	Operational
Ballygrant	NF	150	WoSWA	PCI	1998	Operational
Balquhidder	NF	100	ESWA	PCI	1998	Operational
Banwell	UF	6,000	Bristol W	Kalsep	2001	Operational
Bonar Bridge	NF	1,100	NoSWA	Koch/FS	2000	Operational
Bracadale	NF	190	NoSWA	Koch/FS	1996	Operational
Brif O'Turk	NF	150	ESWA	PCI	1999	Operational
Broadford	NF	705	NoSWA	Koch/FS	1999	Operational
Bunessan	NF	550	WoSWA	Koch/FS	1996	Operational
Bunwell	RO	400	Anglian	Koch/FS	1997	Operational
Carradale	UF	360	WoSWA	Hydronautics	??	In supply
Carrick Castle	NF	70	WoSWA	PCI	1998	Operational
Carrshield	UF	80	NWL	Kalsep	2000	Operational
Carsphairn	NF	47	WoSWA	PCI	2001	Operational
Charterhouse	UF	2,000	Bristol W	Kalsep	2001	Operational
Cladich	NF	20	WoSWA	PCI	1994	Operational
Clay Lane	UF	160,000	Three Vall. W	Norit/X-flow	2001	Operational
Colonsay	NF	123	WoSWA	PCI	2000	Operational
Cornhow	MF	35,000	United Utilities	USF	2000	Operational
Corrie	NF	190	WoSWA	PCI	1999	Operational
Craighouse	NF	80	WoSWA	PCI	2001	Operational
Crathie	MF/UF	240	??	USF	??	Operational
Crianlarich	NF	250	ESWA	PCI	1999	Operational
Crug	UF	3,000	Welsh W	Norit/X-flow	2001	Operational
Crumpwood	UF	7,400	South Staffs W	Kalsep	2002	Operational
Dagenham	RO	4,700	Essex & Suff	Koch/FS	1997	Mothballed
Dalmally	NF	470	WoSWA	Koch/FS	2000	Operational
Dalwhinnie	NF	150	NoSWA	PCI	2001	Operational
Debden Rd	BWRO	6,000	Three Valleys	Koch/FS	2000	Operational
Dervaig	NF	150	WoSWA	PCI	1997	Operational
Dolbenmaen	UF	5,000	Welsh W	Norit	2002	Operational
Ennerdale	MF/UF	59,000	United Utilities	USF	1999	Operational
Eredine	NF	25	WoSWA	PCI	1996	Operational
Flag Fen	RO	1,440	Anglian W	Koch/FS	2000	Operational
Forum	UF	2,000	Bristol W	Kalsep	2001	Operational
Frome	UF	5,000	Bristol W	Kalsep	2001	Operational
Gigha	NF	140	WoSWA	PCI	2002	Operational
Gorthleck	NF	443	NoSWA	PCI	1998	Operational
Gwastadgoed	UF	1,000	Welsh W	Norit/X-flow	2002	Operational
Halton-lea-gate	UF	210	NWL	Kalsep	2000	Operational

Location	**Type**	**Capacity m³/d**	**Client**	**Membrane supplier**	**Date**	**Status**
Homesford	MF/UF	65,000	??	USF	??	Operational
Hook	UF	2,400	South West W	Norit/X-flow	2002	Operational
Houndall	UF	4,500	South West W	Norit/X-flow	2001	Operational
Huntington	C/UF	80,000	United Utilities	USF/Acum.	1998	Standby
Ilseornsay	NF	150	NoSWA	PCI	2001	Operational
Inverasdale	NF	200	NoSWA	Koch/FS	2000	Operational
Inverness	C/UF	34,000	NoSWA	Norit/X-flow	2002	Commiss.
Jersey	SWRO	6,000	JNWC	Toray	1997	Operational
Keldgate	UF	90,000	Yorks W	Norit/X-flow	2001	Operational
Kepwick	UF	2,000	Yorks W	Norit/X-flow	1998	Operational
Kilberry	NF	10	WoSWA	PCI	1998	Operational
Kilham	RO	1500	Yorkshire W	Koch/FS	1998	Operational
Killin	NF	200	ESWA	PCI	1999	Operational
Kirkmichael	NF	120	NoSWA	PCI	1995	Operational
Kyle	NF	1700	NoSWA	Koch/FS	2001	Operational
Laggan Bridge	NF	20	NoSWA	PCI	2001	Operational
Locheamhead	NF	300	ESWA	PCI	2002	Commiss.
Lochgair	NF	70	WoSWA	Koch/FS	1992	Mothballed
Lochgoilhead	NF	136	WoSWA	PCI	2001	Operational
Lochranza	NF	310	WoSWA	PCI	1999	Operational
Lye Oak	MF	7,500	Folks.& Dov.	Memcor	2002	Operational.
Mallaig	NF	1500	NoSWA	Koch/FS	2002	Commiss.
Millenm. Dome	UF RO	500	Millenn. Dome Commission	Norit/X-flow Koch/FS	2000	Mothballed
Nth. Orpington	UF	9,100	Thames W	Norit/X-flow	2001	Operational
Nth. Pickenham	RO	1,600	Anglian Water	Koch/FS	1997	Mothballed
Oldford	UF	15,000	Bristol W	Kalsep	2002	Operational
Ottinge	MF	3,500	Folks.& Dov.	Memcor	2002	Operational.
Pen-Y-Bont	UF	2,500	Welsh W	Norit/X-flow	2002	Operational
Raasay	NF	200	NoSWA	PCI	2001	Operational
Rushall	RO	2,400	Anglian W	Koch/FS	1997	Operational
Scilly Ilses	RO	100	Municipal.	Toray		Operational
Sherbome	UF	4,000	Bristol W	Kalsep	2001	Operational
Slaggyford	UF	250	NWL	Kalsep	2000	Operational
St Aidans	RO	2,000	Yorkshire W	Koch/FS	1996	Dismantled
Strollamus	NF	100	NoSWA	PCI	2001	Operational
Teangue	NF	350	NoSWA	Koch/FS	2001	Operational
Tomnavoulin	NF	100	NoSWA	PCI	1995	Operational
Trecastell	UF	3,500	Welsh W	Norit/X-flow	2002	Commiss.
Tyn-y-Waun	UF	10,000	??Hyder	Aquasource	??	Operational
West Stonedale	MF/UF	800	Yorkshire Water	Norit/X-flow		Operational
Whitebull	C/UF	45,000	United Utilities	USF	1998	Standby
Wilmington	UF	3000	South West W	Norit/X-flow	2001	Operational
Winwick	MF/UF	16,000	United Utilities	USF	1997	Standby
TOTAL		**725,471**				

C/UF: Coag + UF. BWRO, SWRO: Brackish Water, Sea Water RO.

ESWA, NoSWA, WSWA: East, North and West of Scotland Water Authorities respectively; Folks.& Dov., Folkstone and Dover; JNWC Jersey New Waterworks Council; MM Mott MacDonald; NWL Northumberland Water Limited

Koch/FS: Koch/Fluid Systems. WES: Water Engineering Services

http://www.cranfield.ac.uk/sims/water/mem-net/uk_membrane_municipal_plant.html (2003)