CRANFIELD UNIVERSITY

David Christopher Metcalfe

Application of Suspended Ion Exchange, In-line Coagulation and Ceramic Membranes for Surface Water Treatment

School of Energy, Environmental Technology and Agrifood
MSc by Research

Master of Science
Academic Year: 2014 - 2016

Supervisor: Dr. Peter Jarvis
April 2016

CRANFIELD UNIVERSITY

School of Energy, Environmental Technology and Agrifood
MSc by Research

Master of Science

Academic Year: 2014 - 2016

David Christopher Metcalfe

Application of Suspended Ion Exchange, In-line Coagulation and Ceramic Membranes for Surface Water Treatment

Supervisor: Dr. Peter Jarvis
April 2016

This thesis is submitted in partial fulfilment of the requirements for the degree of Master of Science by Research

© Cranfield University 2016. All rights reserved. No part of this publication may be reproduced without the written permission of the copyright owner.

ABSTRACT

A long term, large scale pilot study was performed to assess the use of a novel process based on suspended ion exchange (SIX®) and in-line coagulation (ILCA®) pretreatment for ceramic membrane filtration (CeraMac®), for treating three variable quality UK surface waters.

SIX was shown to remove similar quantities of dissolved organic carbon (DOC) to coagulation for low to moderate DOC source waters. However, during periods of high DOC concentrations and high specific UV absorbance, the removal of organic compounds was reduced. The long term DOC removal data for the SIX process indicated good performance, which was in line with previously reported results from studies using other suspended ion exchange processes.

Organic characterisation using liquid chromatography–organic carbon detection (LC-OCD) revealed the differing selectivities of the SIX and ILCA processes, for low and high molecular weight organic fractions respectively. When these processes were used in combination, a broad range of organic compounds were removed, leading to a 50% reduction in DOC concentration in comparison with an existing full scale conventional treatment process. Subsequently, disinfection by-product (DBP) formation was significantly reduced (62% vs. the conventional process) due to the lower DOC concentration, reduced specific reactivity of the residual organic compounds and reduced formation of brominated DBPs.

Removal of high molecular weight organic compounds (biopolymers) was shown to be critical for stable operation of ceramic membranes at high flux. Optimised in-line coagulation (ILCA) pretreatment (which flocculated the biopolymers) led to negligible membrane adsorption of organic compounds, as low molecular weight (LMW) fractions (which are recalcitrant to coagulation) were shown not to be retained by the membrane. Due to this, when using optimised ILCA, additional removal of LMW organic fractions by using SIX in combination with ILCA provided no measureable benefit with regards to membrane fouling suppression.

Automation of coagulant dosing was achieved for the high SUVA waters tested, using simple feed forward control based on the UV transmittance of the feed water. The application of this automated system led to very low membrane fouling rates (0.24kPa/day), despite highly challenging operating conditions of elevated fluxes (185 L m^{-2} h^{-1}) and highly variable feed water dissolved organic carbon concentrations (1-10mg/l).

Keywords:

Disinfection by-products; Natural organic matter; Ceramic membrane fouling; Pretreatment; Suspended Ion Exchange; In-line coagulation; Liquid chromatography-organic carbon detection.

ACKNOWLEDGEMENTS

Firstly I would like to acknowledge my employer South West Water (SWW), for financially supporting this study and for providing me with a fantastic opportunity to undertake a Master of Science by Research. Special acknowledgement goes to Chris Rockey whose vision helped to make this project happen and whose support and enthusiasm throughout the project has been of great help, as has his introduction to some outstanding continental beers on the journey!

I would especially like to thank my excellent project supervisor, Dr. Peter Jarvis whose continuous support, patience, guidance and valuable contributions have made the completion of this thesis possible. Thanks also go to Prof. Simon Judd whose valuable guidance and input throughout the project was hugely appreciated.

I would also like to thank the Research and Development team at PWN Technologies who provided invaluable technical, operational and moral support throughout the project, especially, Gilbert Galjaard, Holly Shorney-Darby, Harry Scheerman and Jumeng Zheng.

A debt of gratitude goes to Milo Mackin, who worked tirelessly to keep the pilot operating smoothly whilst I was away and to the SWW laboratories, water quality and operational teams for their support throughout the study. The support of the Interreg 2 Seas program and specifically the DOC2C's project is also gratefully acknowledged.

Finally, I want to thank my fantastic family and friends for keeping me sane and most of all, a huge thank you goes to my partner Sophie for her endless patience and support whilst I completed my MSc – you have been a star.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF EQUATIONS

LIST OF ABBREVIATIONS

AMP	Asset management period
APHA	American Public Health Association
Br-DBP	Brominated disinfection by-product
BV	Bed volume
BW	Backwash
CDOC	Chromatographable dissolved organic carbon
CEB	Chemically enhanced backwash
CIP	Cleaning in place
CMF	Ceramic microfiltration
DOC	Dissolved organic carbon
DBP	Disinfection by-product
DBPFP	Disinfection by-product formation potential
DPD	N-N-diethyl-p-phenylenediamine
FIX	Fluidised ion exchange
HAA	Haloacetic acid
HAAFP	Haloacetic acid formation potential
HPSEC	High performance size exclusion chromatography
IEX	Ion exchange
ILCA	In-line coagulation
IR	Irreversible
HMW	High molecular weight
HS	Humic substance
LC-OCD	Liquid chromatography – organic carbon detection
LMH	L/(m^2h)
LMW	Low molecular weight
LMW-N	Low molecular weight neutral
LORIV	Lowland river (River Tamar)
MIEX	Magnetic ion exchange
MLD	Mega litres per day
NOM	Natural organic matter
NTU	Nephelometric turbidity unit
OCD	Organic carbon detection
OND	Organic nitrogen detection
OPEX	Operational expenditure
PAC	Powdered activated carbon
RGSF	Rapid gravity sand filtration
SIX	Suspended ion exchange
SUVA	Specific ultraviolet absorbance
SWW	South West Water

THM	Trihalomethane
THMFP	Trihalomethane formation potential
TMP	Trans-membrane pressure
TOC	Total organic carbon
UPRES	Upland reservoir (Burrator Reservoir)
UPRIV	Upland river (River Tavy)
UV	Ultraviolet
UVA	Ultraviolet absorbance at 254nm (typically following 0.45µm filtration)
UVD	Ultraviolet detection
UVT	Ultraviolet transmittance at 254nm (typically following 0.45µm filtration)
WTW	Water treatment works
WWTW	Waste water treatment works

1 Introduction

1.1 Background

Historically, conventional processes consisting of coagulation, clarification and granular media filtration have been used as the main pretreatment of surface water, to remove dissolved organic carbon (DOC) and particles from water to provide a high quality treated water suitable for disinfection (Bolto *et al.* 2004; Bond *et al.* 2011). These processes require significant intervention and optimisation to provide sufficient removal of natural organic matter (NOM) and to destabilise particles suitably for effective removal by granular media filters. Due to this, conventional WTW processes were typically operated and managed by dedicated local teams. However, the water industry is moving towards increased efficiency via automation, remote monitoring of processes and the use of multi-skilled mobile workforces, which may not be as well suited to this type of treatment process.

The concentration of DOC in UK surface waters has been shown to have increased significantly over the last few decades (Matilianen et al. 2010; Ritson et al. 2014), linked to reduced acid deposition, elevated temperature, changes in land use, altered precipitation patterns and increased frequency of extreme weather events associated with climate change. A study by Evans *et al*. (2005) showed that the average DOC concentration of 22 UK surface waters increased by 91% over a 15 year period. Changes in the nature of the dissolved organics have also been noted, which can affect their removal by water treatment processes (Eikebrokk et al. 2004; Fearing *et al.* 2004; Hurst *et al.* 2004; Sharp *et al.* 2006). In addition to these long term trends, increased incidence and magnitude of rapid changes in the quantity and characteristics of the organic compounds within water sources has been observed, as a result of more frequent extreme climatic events.

These factors may challenge the ability of conventional processes to constantly produce treated water which is suitable for effective disinfection (free from chlorine resistant pathogens such as *Cryptosporidium* and low in turbidity and

NOM) without excessive formation of disinfection by products. This is because low molecular weight (LMW) / hydrophilic organic fractions are typically recalcitrant to coagulation processes (Fabris *et al.* 2007; Humbert *et al.* 2007) therefore, increases in these fractions in the raw water lead to increased treated water DOC concentration. In addition, rapid changes in DOC and high DOC concentrations can have detrimental effects upon conventional treatment processes, leading to increased particle breakthrough when using conventional granular filtration (Hurst *et al.* 2004).

Innovative water treatment processes may offer benefits over conventional treatment, allowing improvements in treated water quality and efficiency of production to meet rising customer and regulatory expectations.

The application of membrane processes has increased within water treatment (Huang *et al.* 2012) due to some potentially key advantages over granular media filtration including: compact footprint, simplified (automated) operation, robustness against fluctuating feed water quality, improved treated water quality and the provision of an absolute barrier to suspended particles and pathogens such as *Cryptosporidium* (Mo & Huang. 2003; Vreeburg *et al.* 2008; Huang *et al.* 2009). Polymeric membranes have been utilised most commonly for water treatment; however, ceramic membrane processes have received increased interest over the last two decades.

Ceramic membranes offer advantages over polymeric materials such as greater operational lifetime, increased solids loading capacity, higher sustainable flux rates (due to reduced organic fouling), increased mechanical robustness and resistance to aggressive cleaning protocols (Kommineni *et al.* 2010; Hofs *et al.,* 2011; Lee & Kim, 2014). These benefits, along with advancements in ceramic membrane filtration (CMF) systems, have meant that the higher initial capital costs associated with these membranes can be largely offset by significantly higher flux rates and lower operating costs over the life of the installation, making ceramic membranes potentially cost competitive on a whole life cost basis (Meyn *et al.* 2012; Lee *et al.* 2013; Shang *et al.* 2015).

Regardless of membrane material, a major obstacle to their wide scale application is membrane fouling which occurs when particulate or dissolved compounds are adsorbed to the membrane structure, leading to reduced permeability (Huang *et al.* 2009). Research has thus focussed on the causes of membrane fouling, with organic fouling being identified as the most significant factor for membrane filtration of surface waters. Further research has involved utilising pre-treatment, such as coagulation, adsorption, oxidation or pre-filtration stages, to remove highly fouling organic material and reduce membrane fouling (Fabris *et al.* 2007; Humbert *et al.* 2007; Huang *et al.* 2009; Myat *et al.* 2012; Huang *et al.* 2015). Whilst high molecular weight (HMW) organic compounds and colloids are widely recognised as being a significant cause of membrane fouling (Fan *et al.* 2008; Dramas & Croué, 2013; Tian *et al.* 2013; Kimura *et al*. 2014; Yamamura *et al.* 2014), the contribution of low MW (LMW) organic compounds is less clear (Carroll *et al.* 2000; Bessiere *et al.* 2009; Gray *et al.* 2011).

In addition to preventing membrane fouling, the removal of natural organic matter (NOM) and its dissolved constituents (i.e. DOC) is often essential to improve the aesthetic quality of the treated water, reduce its capacity for biological regrowth and reduce negative effects on downstream processes such as ultraviolet (UV) light disinfection, advanced oxidation processes (AOP) and granular activated carbon (GAC) filtration (Cornelisson *et al,* 2008). It is also extremely important for reducing by-products formed during chemical disinfection. Chlorine is the most commonly used disinfectant in water treatment (Sadiq & Rodriguez, 2004; Bond *et al.* 2012) and reacts with residual NOM, forming a wide range of unwanted disinfection by-products (DBPs), some of which are potentially harmful to human health (Mergen *et al.* 2009; Bond *et al.* 2012; Richardson & Ternes, 2014).

Coagulation has been the most commonly applied process for NOM removal (within conventional water treatment processes). However, anion exchange processes have been identified as an efficient alternative or supplementary process to other NOM removal processes (such as coagulation, activated carbon filtration etc.) (Bolto *et al.* 2004; Bond *et al.* 2011; Watson *et al.* 2015). Anion exchange resins can remove a portion of the NOM present in source water due to the negative charge carried by most organic compounds. Historically, these resins have been primarily used within a fixed bed configuration (Drikas *et al.* 2002; Cornelisson *et al*, 2009), which has limited their use to low turbidity sources such as ground waters. To overcome this problem, systems which use fluidised or suspended ion exchange have been developed (Drikas *et al.* 2002; Cornelisson *et al*, 2009; Galjaard *et al.* 2011) for application to surface waters which contain higher concentrations of suspended material.

The Magnetic Ion Exchange (MIEX – Ixom Watercare, Australia) system is one such suspended ion exchange (IEX) process which has been used for the removal of DOC since 2001 within a number of full scale plants. This process has typically been applied preceding conventional coagulation and granular media filtration processes to enhance NOM removal (Drikas *et al.* 2003; Fearing *et al.* 2004; Mergen *et al.* 2008 & 2009). More recently, the suspended ion exchange (SIX) process (PWN Technologies, Netherlands) has been developed for the removal of DOC and other anions from surface waters (Galjaard *et al.* 2011). The key novelty of this process is that a single pass plug flow system is employed, meaning that only freshly regenerated resin is contacted with the raw water for a known period of time (whereas MIEX returns 90-95% of resin without regeneration). This provides favourable adsorption kinetics and reduces the opportunity for resin blinding and bio-fouling. In addition, since most commercially available resins can be used within the process, the resin can be selected based on the characteristics of the organic compounds present in the raw water.

1.2 Research motivation

The motivation for this research project was related to South West Water's (SWW) long term strategic goal to build a new water treatment works (WTW) to replace the existing Crownhill WTW (90 mega litre per day (MLD), Plymouth, UK). During preparations for asset management period (AMP) 6, SWW reviewed and restated drinking water treatment goals for new WTWs to include:

- Provision of an absolute barrier to *Cryptosporidium.*
- Enhancement of water quality, particularly DOC removal, DBP reduction and effective removal of pesticide risks where present.
- Use of efficient design to realise improved operability (compact footprint, automation, reliability and robustness of processes).
- Sustainability (chemicals, energy, waste, life expectancy).
- Application of innovative, forward looking technology where applicable.

The two primary goals for the selection of treatment processes for the new WTWs were driven by changes in UK Regulations and consumer expectations with respect to drinking water quality; to provide an absolute barrier to *Cryptosporidium* and reduce DOC and DBP formation. These goals were in part related to the company's reliance on surface waters (95% surface water abstraction), the increasing challenge from raw water organic compounds and elevated *Cryptosporidium* risk related to the agricultural environment. Following a review of process options, the SIX® ILCA® CeraMac® process (suspended ion exchange, in-line coagulation, ceramic membrane filtration, (PWN Technologies, Netherlands)) was identified as a promising technology which could potentially better meet SWWs goals compared to conventional processes.

PWN Technologies had previously researched the application of ceramic membranes for several years prior to implementation at full scale, developing the CeraMac® process itself and optimising pretreatment during this period (Galjaard *et al.* 2011). The CeraMac® system allows up to 200 25m^2 ceramic membrane elements (Metawater, Japan) to be housed in one vessel, allowing simultaneous backwash, reducing the materials and valves required and improving the economics of ceramic membrane use. PWN Technologies also found that that the use of IEX pretreatment improved operation and better met their goals compared to coagulation, subsequently developing the SIX® process. The SIX® CeraMac® process was piloted for a significant period prior to being implemented at full scale at the Andijk III WTW (120MLD, Andijk, Netherlands, PWN) in 2014, replacing the existing conventional pretreatment processes.

Due to the novelty of these processes SWW obtained a 150m^3/day pilot plant to allow long term pilot testing, to assess the application of these technologies to the three different raw water sources that supply Crownhill WTW.

1.3 Research Gap

Blind literature surveys were conducted using the search engine Scopus, with the number of publications per year relating to aspects of the research being assessed between 1991 and 2015.

The search terms “ceramic membranes” and “water treatment” were applied to titles, abstracts and keywords and the results are shown in Figure 1.1. These data indicate growing interest in the use of ceramic membranes, particularly since 2007. In 2015 the number of published papers nearly doubled compared to previous years suggesting a recent surge in interest potentially related to the recent completion of several large scale ceramic membrane water treatment plants (Yokohama - 171MLD, Andijk – 120MLD, Colorado – 37MLD) and growing recognition of the potential operational and life cycle cost benefits of using ceramic membranes.

The total number of ceramic membranes papers retrieved was however only 370 compared to 11109 when the search terms were adjusted to “membranes” and “water treatment” which indicates the marginal nature of ceramic membrane research.

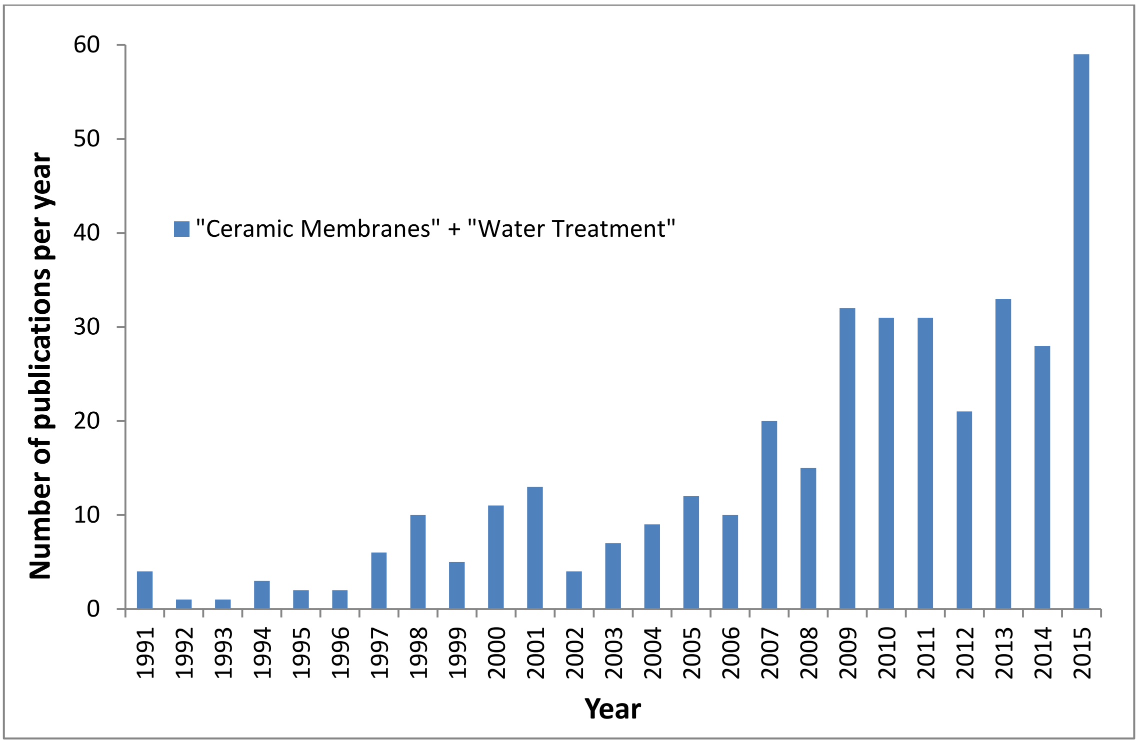

Figure 1.1 Number of publications per year using the search terms "water treatment" and "ceramic membranes" for the period 1991-2015 (Scopus).

A further search was conducted to assess the number of publications per year related to membrane fouling in water treatment applications associated with the pretreatments; coagulation, ion exchange and combined coagulation and ion exchange (Figure 1.2 – search terms are displayed within the figure). The results indicate that coagulation was by far the most commonly investigated pretreatment (289 results), the number of reported studies increasing gradually over the 25 year search period. The use of ion exchange only returned approximately 20% the number of results compared to coagulation (63 results). Combined ion exchange and coagulation returned only approximately 6% the number of results compared to coagulation (16 results). This highlights the relatively limited research on the use of ion exchange pretreatment (or combined ion exchange / coagulation) compared to coagulation pretreatment for membrane filtration. These data also indicate that in general, research into pretreatments for membrane filtration has increased, particularly since the late 1990s, possibly reflecting increased awareness of the significance of *Cryptosporidium* in water supplies and recognition that membrane processes provide a method for increasing the robustness of *Cryptosporidium* removal. This can be attributed to several significant *Cryptosporidium* outbreaks in the 1990s and subsequent reviews (Badenoch 1990 & 1995, Bouchier 1998). These reviews highlighted that where conventional processes are inadequate or become compromised, *Cryptosporidium* oocysts may pass into the treated water in significant numbers leading to a risk of outbreaks or illness within the community.

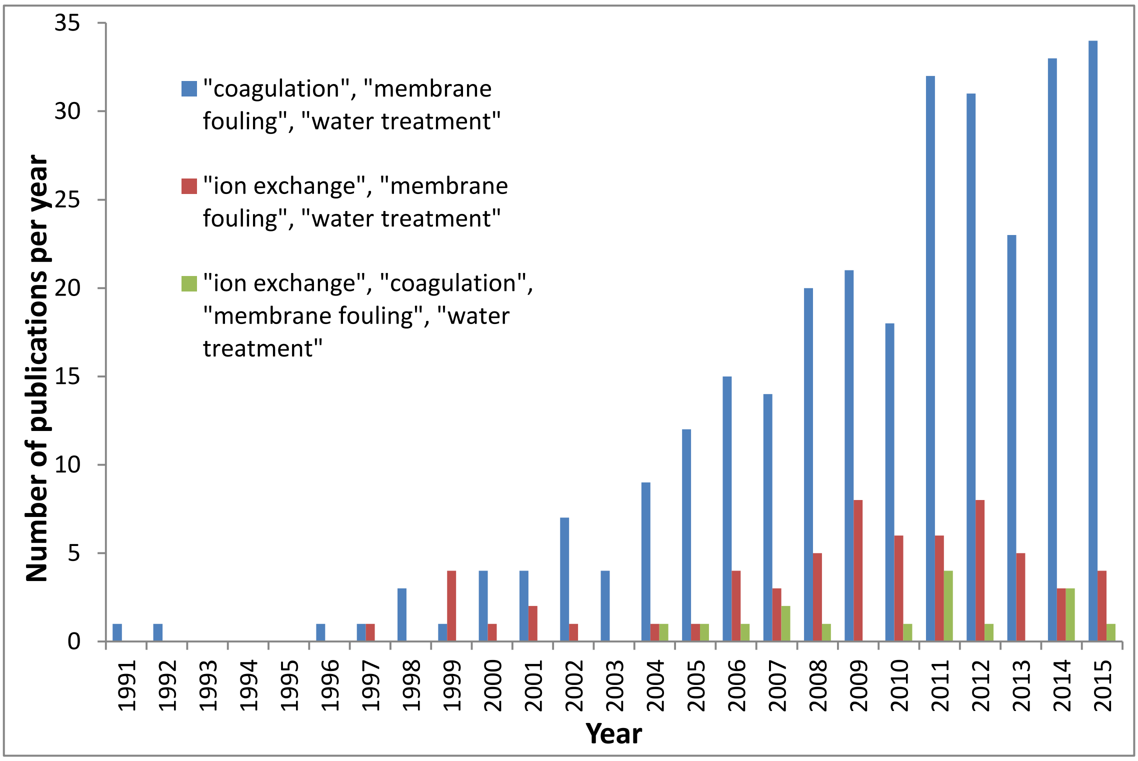

Figure 1.2 Number of publications per year considering the search terms "membrane fouling" and "water treatment" with either "coagulation", "ion exchange" or "coagulation" and "ion exchange" for the period 1991-2015 (Scopus).

Whilst 241 papers have been published relating to the use of MIEX, the number of peer reviewed publications relating to SIX is limited with much of the research being completed by the research group of PWN Technologies. Many of the MIEX published trials (approximately 85%) have however been performed at bench scale using non-standard operational conditions which may be misleading for full scale application; Walker and Boyer (2011) found that DOC removal by MIEX decreased by 24% after only 21 regeneration cycles and Mergen *et al.* (2008) found that DOC removal could decline from 60% to 25% when MIEX was reused under the typical operational conditions of a full scale process.

This research is the first of its kind to evaluate the use of combined IEX (in this case SIX) and coagulation pretreatment for ceramic microfiltration. Research was performed using three UK surface waters and a relatively large scale pilot plant (150m^3/day), operated over an extended period (2 years) to provide relevant, long term information for the full scale application of these processes for water treatment. Outcomes have been published in the peer reviewed literature (Metcalfe *et al*. 2015 & 2016).

1.4 Aims and Objectives

The overriding aim of the research was to assess the use of the SIX/ILCA/CeraMac process for the treatment of three variable quality surface waters, with several specific objectives, including:

- Establish the removal of dissolved organic carbon (DOC) and individual organic fractions by different treatment processes as determined by liquid chromatography – organic carbon detection (LC-OCD). Compare the LC-OCD results for the pilot plant processes (SIX/ILCA/CeraMac) against conventional treatment processes.
- Understand the effect of different treatment processes on DBP formation potential (DBPFP), relating any differences to the residual organic compounds present and other water quality parameters. Compare the results for the pilot plant processes against conventional treatment processes.
- Understand the mechanism of ceramic membrane fouling associated with the residual organic fractions present following different pretreatments.

- Determine the suitability of any devised process solution (including ceramic membranes) for full scale water treatment and any benefits or drawbacks in comparison with conventional treatment.

1.5 Thesis Structure

This thesis is presented in the form of two papers followed by an overall discussion and conclusions. Chapter 2 reports the results of investigations into DBP precursor removal by SIX or a combined SIX and in-line (ILCA) coagulation process prior to CMF (pilot scale), in comparison with a full scale conventional treatment works using optimised coagulation. This paper has been published in Water Research (Metcalfe *et al*. 2015). Chapter 3 reports the results of a study which investigated the suppression of irreversible ceramic membrane fouling, associated with the organic fractions removed by pretreatments including; SIX, coagulation / clarification, combined coagulation / clarification and SIX, combined SIX and ILCA and ILCA alone. This paper has been published in Separation and Purification Technology (Metcalfe *et al.* 2016). An overall discussion, conclusions and recommendations for further research are contained in Chapter 4, 5 and 6 respectively.

1.6 References

Badenoch, J. (1990). *Cryptosporidium* in water supplies. Report of the Group of Experts; Department of the Environment, Department of Health. London, UK. HMSO.

Badenoch, J. (1995). *Cryptosporidium* in water supplies. Second Report of the Group of Experts; Department of the Environment, Department of Health. London, UK. HMSO.

Bouchier, I. (1998). *Cryptosporidium* in water supplies: Third Report of the Group of Experts. Department of Health. London, UK. HMSO.

Bessiere, Y., Jefferson, B., Goslan, E., Bacchin, P., 2009. Effect of hydrophilic / hydrophobic fractions of natural organic matter on irreversible fouling of membranes. *Desalination,* 249(1), pp. 182-187.

Bolto, B., Dixon, D., Eldridge, R., 2004. Ion exchange for the removal of natural organic matter. *Reactive and Functional Polymers,* 60(1-3), pp. 171-182.

Bond, T., Goslan, E., H., Parsons, S., A., Jefferson, B., 2011. Treatment of disinfection by-product precursors. *Environmental. Technology*. 32 (1), 1-25.

Bond, T., Goslan, E.H., Parsons, S. A., Jefferson, B., 2012. A critical review of trihalomethane and haloacetic acid formation from natural organic matter surrogates. *Environmental Technology Reviews,* 1 (1), pp 93–113.

Boyer, T.H., Singer, P.C., 2005. “Bench-scale testing of a magnetic ion exchange resin for removal of disinfection by-product precursors”, *Water Research,* 39, pp 1265-1276

Carroll, T., King, S., Gray, S.R., Bolto, B.A., Booker, N.A., 2000. The fouling of microfiltration membranes by NOM after coagulation treatment. *Water Research,* 34(11), pp. 2861-2868.

Chow, C., Fabris, R., Cook, D., Drikas, M., 2004. Evaluation of Treatment Systems for Removal of Natural Organics, *Research Report 23*, The Cooperative Research Centre for Water Quality and Treatment, Salisbury, South Australia

Cornelissen, E.R., Moreau, N., Siegers, W.G., Abrahams, A.J., Rietveld, L.C., Grefte, A., Dignum, M., Amy, G., Wessels L.P., 2008. “”Selection of anionic exchange resins for removal of natural organic matter (NOM) fractions”, *Water Research,* 42, pp 413 – 423

Dramas, L. and Croué, J.-P., 2013. Ceramic membrane as a pretreatment for reverse osmosis: Interaction between marine organic matter and metal oxides. *Desalination and Water Treatment,* 51(7-9), pp. 1781-1789.

Drikas, M., Morran, J.Y., Pelejanic, C., Hepplewhite, C., Bursill, D.B., 2002. Removal of natural organic matter - A fresh approach. *Water Science and Technology; Water Supply*, 2 (1), pp 71–79.

Drikas, M., Chow, C.W.K., Cook, D., 2003. The impact of recalcitrant organic character on disinfection stability, trihalomethane formation and bacterial regrowth: an evaluation of magnetic ion exchange resin (MIEX®) and alum coagulation. *Journal of Water Supply Research and Technolology: AQUA* 52 (7), 475-487.

Drikas, M., Dixon, M., Morran, J., 2011. “Long term case study of MIEX pre-treatment in drinking water; understanding NOM removal”, *Water Research*, Vol. 45, pp 1539-1548

Evans, C. D., Monteith, D. T., Cooper, D.M., 2005. Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. *Environmental Pollution,* 137 (1), pp. 55-71.

Fabris, R., Lee, E.K., Chow, C.W.K., Chen, V., Drikas, M., 2007. Pre-treatments to reduce fouling of low pressure micro-filtration (MF) membranes. *Journal of Membrane Science,* 289 (1-2), pp. 231-240.

Fan L., Nguyen T., Roddick, F.A., Harris, J.L., 2008. Low-pressure membrane filtration of secondary effluent in water reuse: Pre-treatment for fouling reduction. *Journal of Membrane Science,* 320(1-2), pp. 135-142.

Fearing, D.A., Banks, J., Guyetand, S., Eroles, C.M., Jefferson, B., Wilson, D., Hillis, P., Campbell, A.T., Parsons, S.A., 2004. Combination of ferric and MIEX® for the treatment of a humic rich water. *Water Research*, 38 (10), pp. 2551-2558.

Galjaard, G., Martijn, B., Koreman, E., Bogosh, M., Malley, J., 2011. Performance Evaluation SIX® -CeraMac® in Comparison with Conventional Pre-treatment Techniques for Surface Water Treatment. *Water Practice and Technology*, 6 (4).

Gray, S.R., Dow, N., Orbell, J.D., Tran, T., Bolto, B.A., 2011. The significance of interactions between organic compounds on low pressure membrane fouling. *Water Science and Technology,* 64(3), pp. 632-639.

Hofs, B., Ogier, J., Vries, D., Beerendonk, E.F., Cornelissen, E.R., 2011. Comparison of ceramic and polymeric membrane permeability and fouling using surface water. *Separation & Purification Technology*, 79, 365-374.

Huang, H., Schwab, K., Jacangelo, J.G., 2009. Pretreatment for low pressure membranes in water treatment: A review. *Environmental Science and Technology,* 43(9), pp. 3011-3019.

Huang, H., Cho, H.-H., Schwab, K.J., Jacangelo, J.G., 2012. Effects of magnetic ion exchange pretreatment on low pressure membrane filtration of natural surface water. *Water Research*. 46 (17), pp. 5483-5490.

Humbert, H., Gallard, H., Jacquemet, V., Croué , J., 2007. Combination of coagulation and ion exchange for the reduction of UF fouling properties of a high DOC content surface water. *Water Research*. 41 (17), pp. 3803-3811.

Hurst, A.M., Edwards, M.J., Chipps, M., Jefferson, B., Parsons, S.A., 2004. The impact of rainstorm events on coagulation and clarifier performance in potable water treatment. *Science of the Total Environment,* 321 (1-3), pp. 219-230.

Jarvis, P., Mergen, M., Banks, J., Mcintosh, B., Parsons, S.A., Jefferson, B., 2008. Pilot scale comparison of enhanced coagulation with magnetic resin plus coagulation systems. *Environmental Science and Technology*, 42 (4), pp. 1276-1282.

Kimura, K., Tanaka, K., Watanabe, Y., 2014. Microfiltration of different surface waters with/without coagulation: Clear correlations between membrane fouling and hydrophilic biopolymers. *Water Research,* 49, pp. 434-443.

Kommineni, S.N., Bryck, J., Stringer, C., Stevens, C., Meyers, N., Karnik, B., Hoffman, R., Sullivan, L., 2010. Evaluation of an emerging water treatment technology: Ceramic membranes. *Water Science and Technology: Water Supply*, 10 (5), pp 765-770

Lee, S.J., Dilaver, M., Park, P.K., Kim, J.H., 2013. Comparative analysis of fouling characteristics of ceramic and polymeric microfiltration membranes using filtration models. *Journal of Membrane Science*, 432, pp. 97-105.

Lee, S. and Kim, J., 2014. Differential natural organic matter fouling of ceramic versus polymeric ultrafiltration membranes. *Water Research,* 48(1), pp. 43-51.

Matilainen, A., Vepsläläinen, M. and Sillanpää, M., 2010. Natural organic matter removal by coagulation during drinking water treatment: A review. *Advances in Colloid and Interface Science,* 159 (2), pp. 189-197.

Mergen, M.R.D., Jefferson, B., Parsons, S.A., Jarvis, P., 2008. Magnetic ion-exchange resin treatment: impact of water type and resin use. *Water Research*, 42 (8-9), pp. 1977-1988.

Mergen, M.R.D., Adams, B.J., Vero, G.M., Price, T.A., Parsons, S.A., Jefferson, B., Jarvis, P., 2009. Characterisation of natural organic matter (NOM) removed by magnetic ion exchange resin (MIEX® Resin) *Water Science and Technology: Water Supply*, 9 (2), pp. 199-205.

Metcalfe D., Rockey C., Jefferson B., Judd S., Jarvis P., 2015. Removal of disinfection by-product precursors by coagulation and an innovative suspended ion exchange process. *Water Research,* 87, pp. 20-28.

Metcalfe, D., Jarvis, P., Rockey, C., Judd, S., 2016. Pre-treatment of surface waters for ceramic microfiltration. *Separation and Purification Technology,* 163, pp. 173-180.

Meyn, T., Altmann, J., Leiknes, T., 2012. In-line coagulation prior to ceramic microfiltration for surface water treatment-minimisation of flocculation pre-treatment. *Desalination and Water Treatment*, 42 (1-3), pp. 163-176.

Mo, L. and Huang, X., 2003. Fouling characteristics and cleaning strategies in a coagulation-microfiltration combination process for water purification. *Desalination,* 159(1), pp. 1-9.

Myat, D.T., Mergen, M., Zhao, O., Stewart, M.B., Orbell, J.D., Gray, S., 2012. Characterisation of organic matter in IX and PACl treated wastewater in relation to the fouling of a hydrophobic polypropylene membrane. *Water Research,* 46(16), pp. 5151-5164.

Ritson, J.P., Graham, N.J.D., Templeton, M.R., Clark, J.M., Gough, R., Freeman, C., 2014. The impact of climate change on the treatability of dissolved organic matter (DOM) in upland water supplies: A UK perspective. *Science of the Total Environment,* 473-474, pp. 714-730.

Sadiq, R. and Rodriguez, M.J., 2004. Disinfection by-products (DBPs) in drinking water and predictive models for their occurrence: A review. *Science of the Total Environment,* 321(1-3), pp. 21-46.

Shang, R., Vuong, F., Hu, J., Li, S., Kemperman, A.J.B., Nijmeijer, K., Cornelissen, E.R., Heijman, S.G.J., Rietveld, L.C., 2015. Hydraulically irreversible fouling on ceramic MF / UF membranes: Comparison of fouling indices, foulant composition and irreversible pore narrowing. *Separation and Purification Technology,* 147, pp. 303-310.

Sharp, E.L., Parsons, S.A. and Jefferson, B., 2006. The impact of seasonal variations in DOC arising from a moorland peat catchment on coagulation with iron and aluminium salts. *Environmental Pollution,* 140 (3), pp. 436-443.

Richardson, S.D., Ternes, T.A., 2014. Water analysis: emerging contaminants and current issues. *Analytical Chemistry*. 86, pp. 2813-2848.

Singer, P.C., Bilyk, K., 2002. Enhanced coagulation using a magnetic ion exchange resin. *Water Research*. 36 (16), pp. 4009-4022.

Tian, J., Ernst, M., Cui, F., Jekel, M., 2013. Correlations of relevant membrane foulants with UF membrane fouling in different waters. *Water Research,* 47(3), pp. 1218-1228.

Vreeburg J.H.G., Schippers D., Verberk J.Q.J.C., Van Dijk J.C., 2008. Impact of particles on sediment accumulation in a drinking water distribution system. *Water Research,* 42(16), pp. 4233-4242.

Watson, K., Farre, M.J., Knight, N., 2015. Enhanced coagulation with powdered activated carbon or MIEX® secondary treatment: a comparison of disinfection by-product formation and precursor removal. *Water Research*. 68, pp. 454-466.

Yamamura, H., Okimoto, K., Kimura, K., Watanabe, Y., 2014. Hydrophilic fraction of natural organic matter causing irreversible fouling of microfiltration and ultrafiltration membranes. *Water Research,* 54, pp. 123-136.

2 Removal of disinfection by-product precursors using coagulation and an innovative suspended ion exchange process

David Metcalfe[1], Chris Rockey[1], Bruce Jefferson[2], Simon Judd[2,3] and Peter Jarvis[2].

[1]*Science and Water Quality Department, South West Water, Exeter, EX2 7HY, England.*

[2]*Cranfield Water Science Institute, Cranfield University, Bedford, MK43 0AL.*

[3]*Department of Chemical Engineering, Qatar University, Qatar.*

Abstract

This investigation aimed to compare the disinfection by-product formation potentials (DBPFPs) of three UK surface waters (1 upland reservoir and 2 lowland rivers) with differing characteristics treated by (a) a full scale conventional process and (b) pilot scale processes using a novel suspended ion exchange (SIX) process and in-line coagulation (ILCA) followed by ceramic membrane filtration (CMF). Liquid chromatography-organic carbon detection (LC-OCD) analysis highlighted clear differences between the organic fractions removed by coagulation and suspended ion exchange. Pretreatments which combined SIX and coagulation resulted in significant reductions in dissolved organic carbon (DOC), UV absorbance (UVA), trihalomethane and haloacetic acid formation potential (THMFP, HAAFP), in comparison with the SIX or coagulation process alone. Further experiments showed that in addition to greater overall DOC removal, the processes also reduced the concentration of brominated DBPs and selectively removed organic compounds with high DBPFP. The SIX/ILCA/CMF process resulted in additional removals of DOC, UVA, THMFP, HAAFP and brominated DBPs of 50, 62, 62, 62% and 47% respectively compared with conventional treatment.

Keywords: Ceramic membrane filtration, Disinfection by-products,

Ion exchange, Natural organic matter

2.1 Introduction

Optimised coagulation is the standard method for the removal of NOM and is effective in the removal of high molecular weight (HMW), hydrophobic and aromatic NOM compounds (Drikas *et al.* 2003; Fearing *et al.* 2004). NOM that is of low MW (LMW) and hydrophilic in nature is not as amenable to removal by coagulation. It is therefore available to react with chlorine to form unwanted disinfection by-products (DBPs) (Mergen *et al.* 2009), some of which are potentially harmful to human health (Richardson & Ternes, 2014). Water treatment works (WTWs) faced with treating water containing high levels of natural organic matter (NOM), or difficult to remove organic matter, are therefore finding meeting DBP regulatory requirements much more challenging using conventional treatment methods. Various strategies exist for reduction of DBPs in treated waters, such as reducing disinfectant dose, switching disinfection method or reducing DBP levels following disinfection, however, arguably the best method is to reduce the DBP precursor concentration prior to disinfection (Bond *et al.* 2010).

Ion exchange (IEX) is an alternative treatment that has received significant attention recently for removal of DBP precursors. Anionic IEX has been used in fluidised (FIX), suspended (SIX) and magnetic (MIEX) forms for this duty (Boyer & Singer 2005; Mergen *et al.* 2008; Cornellison *et al.* 2009; Gan *et al*. 2013; Watson *et al*. 2015). In many cases it has been shown to achieve very high dissolved organic carbon (DOC) removal, especially relating to charged LMW and hydrophilic organic compounds which can be significant DBP precursors. IEX thus appears to target different organic fractions to coagulation (Bolto *et al.* 2002; Drikas *et al.* 2003; Allpike *et al.* 2005; Mergen *et al.* 2009; Bond *et al.* 2010; Kristiana *et al.* 2010). Furthermore, anionic resins can also remove bromide from water sources (Singer & Bilyk 2002), thereby potentially reducing the propensity for formation of brominated DBPs during disinfection (Hua & Reckhow 2012).

Since IEX and coagulation preferentially remove different organic fractions, combining the processes can enhance reductions in NOM and DBP formation potential (DBPFP) (Watson *et al*. 2015). Implementation of IEX prior to coagulation has also been shown to significantly reduce the coagulant dose required (by 50-60%) as well as increasing the size and strength of coagulant flocs (Jarvis *et al.* 2008). IEX as a pretreatment to membrane separation has also been widely investigated. Particularly for high DOC upland water sources, IEX alone has been shown to have little impact on suppressing membrane fouling unless combined with low coagulant doses (Huang et al. 2012a and b; Kabsch-Korbutowicz & Urbanowska, 2012).

Much of the research into the use of IEX for DBPFP control has focussed on the MIEX process (Singer & Bilyk, 2002; Drikas et al, 2003; Allpike et al. 2005; Mergen et al. 2009).

No similarly rigorous reports of pilot-scale studies of the novel SIX process (PWN Technologies, Netherlands), combined with coagulation, have been presented. The MIEX process uses a proprietary resin and typically returns 90-95% of the separated resin to the process without regeneration (Jarvis et al., 2008). However, the SIX process can use most commercially available resins and is a single pass plug flow system so as to limit resin fouling and provide more stable adsorption kinetics. In this research the SIX process has been assessed upstream of ceramic membrane filtration, a combination which has not been widely researched (Hofs *et al.* 2011; Meyn *et al.* 2012; Lee *et al.* 2013). The aim of this research was therefore to compare the removal of DBP precursors from three different source waters using SIX in combination with coagulation and ceramic membrane filtration at pilot scale, to that achievable by conventional coagulation, clarification and sand filtration. The research was carried out using a large scale pilot facility over an 18 month period to provide representative results for long term operation of the processes.

2.2 Methods and materials

2.2.1 Raw waters

Three raw waters were tested on over the trial, either individually or as a blend. These were:

- An upland reservoir (UPRES) with low turbidity and low/moderate DOC (Burrator Reservoir).
- A soft, upland river (UPRIV), prone to rapid changes in quality following rain, with low to high DOC and low to moderate turbidity (River Tavy).
- A lowland river (LORIV) prone to changes in quality following rain with low to high DOC and turbidity (River Tamar).

The water sources were those that supplied the full scale WTWs, against which the pilot plant processes were compared. Three different water sources (low to high DOC) were treated by the ion exchange system and the WTWs (Tests 1-3). The raw water treated by the pilot plant and the WTWs was the same in all tests other than a minor difference in Test 3. This water was dominated by the upland river source, and the pilot process received the most challenging water (Table 2.1). Water quality data for the three sources investigated are shown in Table 2.2 .

Table 2.1 Summary of process conditions tested in these trials (Tests 1 – 3)

Test Number	**Raw Water**	**WTWs RGSF Pre-treatment**	**Pilot Plant CMF Pre-treatment**
1	100% UPRES	Aluminium coagulation (3.18 mg/L) Al, polyelectrolyte	SIX + aluminium coagulation (ILCA) 0.26 mg/L Al
2	100% LORIV	PAC, aluminium coagulation (3.52 mg/l Al), polyelectrolyte	SIX + aluminium coagulation (ILCA) 1.19 mg/L Al
3^{pilot}	100% UPRIV	N/A	SIX + aluminium coagulation (ILCA) 3.16 mg/L Al
3^{wtws}	85% UPRIV / 15% UPRES	PAC, aluminium coagulation (5.09 mg/L Al), polyelectrolyte	N/A

Table 2.2 Water quality data for the three water sources investigated

Test Number	Water Source	TOC (mg/l)	DOC (mg/l)	UVA (cm^{-1})	SUVA (L/mg.m)	Turbidity (NTU)	Colour (Pt-Co mg/l)	Bromide (mg/l)	pH (pH units)	NO_3^- (mg/l)	Alkalinity as HCO_3^- (mg/l)	Alkalinity as CaCO3 (mg/l)
Test 1	UPRES	1.22	1.10	0.05	4.18	0.36	4.90	29.30	6.60	<1.6	5.00	4.10
Test 2	LORIV	4.00	4.02	0.15	3.68	4.00	18.40	69.00	7.70	5.60	49.00	40.16
Test 3 (Pilot)	$UPRIV^{Pilot}$	5.59	6.02	0.28	4.57	1.20	36.50	26.10	7.30	3.53	20.00	16.39
Test 3 (WTW Blend)	$UPRIV^{WTW}_{Blend}$	5.13	5.32	0.24	4.51	2.50	30.50	NS	7.30	2.92	18.00	14.75

2.2.2 Full scale WTWs process

The WTWs (Crownhill WTWs, South West Water (SWW), Plymouth, U.K) treated water using optimised coagulation with aluminium sulphate dosed at 3.18 to 5.09 mg/L as Al (Kemira, U.K) and *Magnafloc LT25* (BASF, U.K) anionic polyelectrolyte at 0.1-0.2 mg/L (Table 2.1). When treating river waters, powdered activated carbon (PAC, *Aquasorb BP2*, Jacobi, UK) was dosed at 2-3 mg/L prior to coagulation. The WTW's coagulant dose was optimised through jar testing and works operation. Flash mixing, flocculation and sludge blanket clarification was followed by rapid gravity sand filtration (RGSF). RGSF filtrate samples were collected during all tests to allow comparison with the pilot plant process to provide a benchmark for organic matter removal based on optimised coagulation.

2.2.3 Pilot plant process

Experimental work was performed using a containerised pilot plant comprising the SIX®, in-line coagulation (ILCA®) and CMF (CeraMac®) processes (PWN Technologies, Netherlands) and have been described elsewhere (Galjaard *et al.* 2011). A simple flow sheet of the pilot plant is shown in Figure 2.1. The 150 m^3/day pilot plant comprised:

- SIX – an acrylic quaternary amine, gel-type strongly basic anion exchange resin was used in the chloride form over the duration of the trial (Lewatit S5128, Lanxess, Germany) dosed at 18 ml/L with a contact time of 30 minutes, dosing conditions established as suitable for treatment of the water sources in preliminary bench-scale tests. The resin had been in continuous use for 6-18 months when the tests were performed.
- Resin was settled from the treated flow by a lamella separator. Resin was regenerated with 30 g/L NaCl. SIX treated water samples were collected directly after resin separation.
- ILCA using polyaluminium chloride (Water Treatment Solutions, U.K) was used following SIX treatment. Water was pH corrected with NaOH or HCl and injected with coagulant, mixed by a static mixer and flocculated for 3.9 minutes prior to CMF. The coagulation pH was 6.4 for all tests. The coagulant dose was optimised for NOM removal by jar testing. UV absorbance at 254 nm (UVA) was used as the surrogate for NOM removal.
- CMF was carried out using one vertically mounted 25 m^2 ceramic membrane element (Metawater, Japan, nominal pore size 0.1 µm), operating by dead end filtration. The membrane flux was 112 LMH (L/(m^2h)) in all tests.

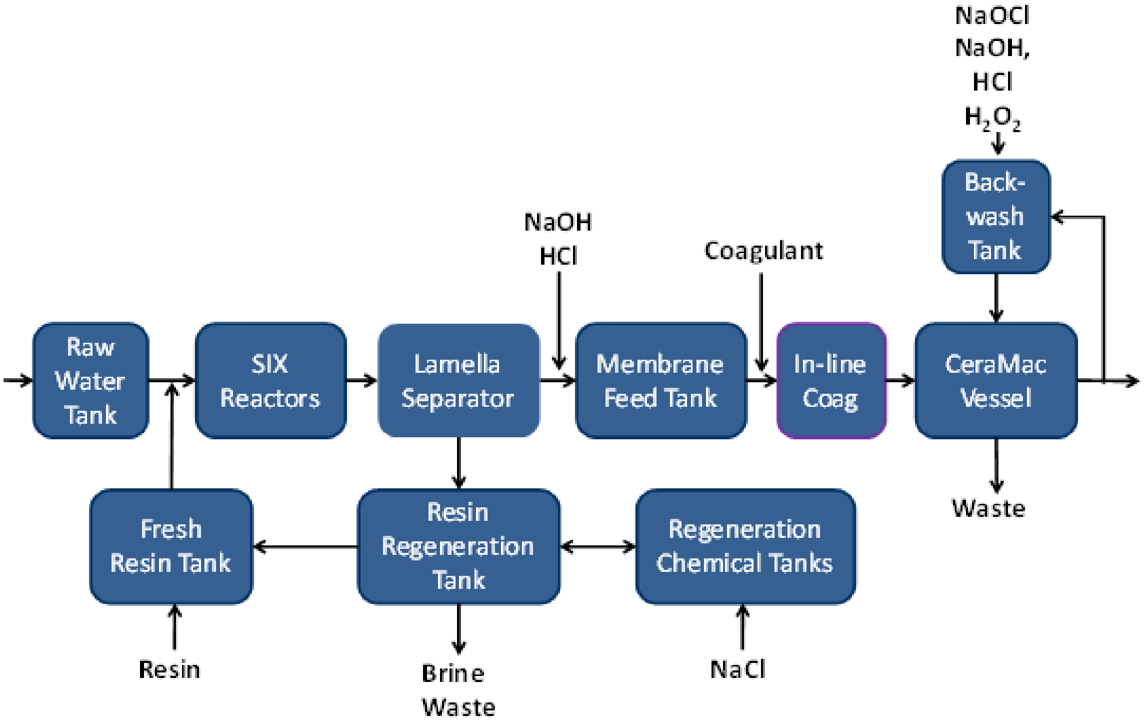

Figure 2.1 Flow sheet for the suspended Ion exchange, in-line coagulation and ceramic membrane filtration pilot plant used in this study

2.2.4 Sample analysis

Samples were collected from the pilot plant and WTWs during stable operation of both systems for the conditions under test. Samples were taken from the pilot plant and WTWs within an hour of one another to ensure direct comparison of the processes treating the same water. UVA was measured using a Hach DR6000 spectrophotometer after samples were filtered through a 0.45 µm filter. Bicarbonate alkalinity was measured by titration using a Metrohm 'Titrandise' system at SWW Laboratories (Exeter, U.K). Bromide was analysed by direct injection ion chromatography (Metrosep A Supp 7-250/4.0 column with a sodium carbonate eluent), using a Metrohm Compact IC Pro at ALS laboratories, Wakefield, U.K. Dissolved organic carbon was measured and characterised using liquid chromatography – organic carbon detection (LC-OCD) at Het Water Laboratorium (Netherlands). This analysis determines the DOC concentration and classifies the CDOC (chromatographable DOC) into a series of different MW fractions classified as biopolymers, humic substances, building blocks, LMW neutrals and LMW acids as described by Huber *et al.* (2011).

THM and HAA formation potential tests (THMFP, HAAFP) were performed at SWW Laboratories using an adapted version of the Standard Method 5710B from the American Public Health Association (APHA) (Eaton *et al.* 2005). All glassware was prepared to ensure it was organic free, PTFE lined caps were used and samples were stored in either amber glass or bottles covered with tin foil. Samples were refrigerated overnight at 4°C and chlorine demand tests were carried out the following day. The N-N-diethyl-p-phenylenediamine (DPD) colourimetric method was used for chlorine measurements and the samples were incubated at 20 °C. Following chlorine demand determination, sample aliquots were buffered at pH 7, dosed with chlorine (ultra-low bromate sodium hypochlorite 14-15%, Brentagg, U.K) and incubated for 7 days at 20 °C. Sample aliquots were tested for residual chlorine and those containing between 3-5 mg/L free chlorine residual were processed for THM and HAA analysis. Triplicate replicates were performed on selected raw water and CMF permeate samples to give an indication of accuracy for the range of waters analysed. All blanks, quality control samples and replicates were well within accepted levels. THM samples were immediately dechlorinated with sodium thiosulphate. HAA samples were immediately preserved with ammonium chloride. Samples were adjusted to a pH <0.5 by the addition of sulphuric acid followed by extraction in 3 ml of methyl tert-butyl ether. The acids were converted to their methyl esters through the addition of acidic methanol and heating for 2 hours at 50 °C. The extract was neutralised by adding a 10% sodium sulphate solution and the solvent layer was analysed for nine HAAs.

The four THMs (chloroform, bromodichloromethane, dibromochloromethane and bromoform) were determined by headspace extraction using a Hewlett Packard 6890/5973N GC-MS system operating in the selected ion mode and fitted with an Agilent 7697A headspace sampler. Nine haloacetic acids (HAA9) were measured using an Agilent 7890A/5975C GC-MS system.

2.3 Results and discussion

2.3.1 Overall water quality

SIX followed by ILCA was compared with conventional treatment for the removal of DOC and DBP precursors from each of the 3 different raw water sources (Tests 1-3). Up to 0.9 mg/L more DOC was removed for SIX/ILCA/CMF compared to that from conventional treatment. Similarly, between 0.007-0.022 cm^{-1} more UVA removal was observed (Figure 2.2). It was observed that no NOM was being removed directly by the membrane itself and that all removal was being achieved by either the SIX or coagulation processes. This was seen from UVA measurements taken from either side of the membrane; in all cases the membrane feed and permeate UVA were almost identical with a less than 0.0009 cm^{-1} difference. Membrane fouling and its amelioration through optimising operation and maintenance forms the subject of another study (Chapter 3). However, the flux was kept constant at 112 LMH and as a result of the optimised pre-treatment membrane fouling was negligible at <3.64 kPa/day. Coagulant dose reductions typically >50% were applied following SIX compared to the full-scale WTWs. Preliminary testing showed that an in-line coagulation contact time of 2 minutes was sufficient for the flocculation of the residual DOC after the SIX stage. This corroborates the conclusions of Meyn *et al.* (2012) who found an in-line flocculation time between 10 and 240 seconds exerted no influence on DOC removal and that 60 seconds was sufficient to generate flocs of low membrane fouling propensity.

The choice between macroporous and gel-type resins for NOM removal is challenged by conflicting outcomes from various studies of resin performance for different resin types when treating NOM-laden waters (Bolto *et al*. 2002; Cornelissen *et al*. 2008). In the current study, the gel-type resin was found to perform well, and was consistent with results reported from studies based on macroporous resins such as MIEX (Drikas *et al.* 2003; Boyer & Singer, 2005; Mergen *et al.* 2009). In Tests 1 and 2, respectively low (1.1 mg/L) and moderate (4.0 mg/L) DOC water sources, the SIX resin dose (18 ml/L) alone was sufficient to provide comparable DOC removal to coagulation. Both water sources were hydrophobic, with SUVA values of 4.2 and 3.7 L/(mg.m) for the low and moderate DOC waters respectively. The DOC removal by SIX was slightly higher than conventional treatment in Test 1 (58 vs. 53%) and 2 (62 vs. 59%). However, removal of the UV-absorbing NOM and organic fractions clearly differed between the processes and for each water source (Figure 2.2). The removal of UVA in comparison to DOC removal by SIX was variable with an additional removal of 10% in Test 1, whilst in Test 2 the removal was -2%. Coagulation gave 25% and 19% more UVA removal compared to DOC in Test 1 and 2, as expected due to the preferential removal of HMW, aromatic NOM noted by previous work (Drikas *et al.* 2003). Combining SIX and ILCA led to significant reductions in UVA with the CMF permeate having less than a third of the UVA of the conventionally treated water in both tests. For some water sources IEX has been found to preferentially remove UV absorbing compounds (Drikas *et al.* 2003; Boyer & Singer, 2005; Shorrock & Drage, 2006), whilst in other cases a neutral or even negative preference for UV absorbing compounds, similar to Test 2, has been reported (Allpike *et al.* 2005; Boyer & Singer, 2006). The variation in reported outputs relate to differences in the NOM composition, the IEX resin type and the available resin surface area, highlighting the need for empirical testing of waters given the complex geographical and temporal variability in organic matter.

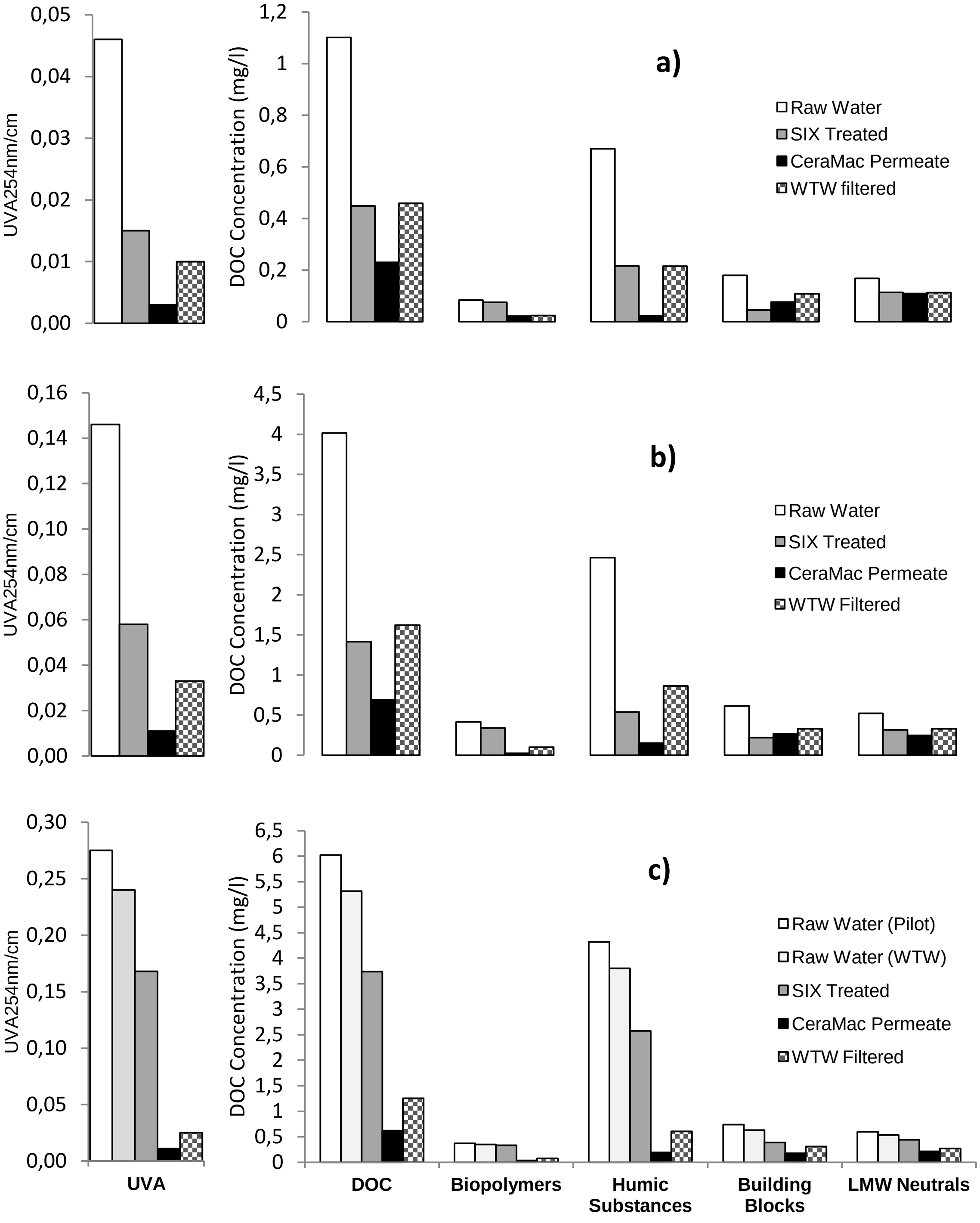

Figure 2.2. UV absorbance, DOC and LC-OCD defined organic fractions removal by SIX, SIX/ILCA/CMF and conventional treatment a) Test 1 - low DOC UPRES, b) Test 2 – moderate DOC LORIV and c) Test 3 – high DOC UPRIV. The LC-OCD reporting limit is 0.2µg/l-C

In Test 3, SIX removed a smaller proportion of the DOC and UVA than for the other source waters (Figure 2.2) which was in part due to the low resin dose for the elevated DOC concentration. Other likely factors, such as competition from inorganic ions and pore blocking by HMW NOM contributed to the reduced removal of DOC. Sulphate has been shown to compete with organic compounds for IEX sites leading to reduced adsorption of DOC (Boyer & Singer, 2006). In this water, the HMW NOM load was much greater (Figure 2.2 and Table 2.2) and the sulphate concentration was more than double that of previous tests with 26mg/l compared to 3mg/l and 10.3mg/l in Tests 1 and 2 respectively. Fearing *et al.* (2004) recorded reduced removal of DOC by IEX following heavy rainfall attributed to pore blockage by higher MW organic compounds. Similarly, Mergen *et al.* (2008) found that the HMW aromatic NOM present in high SUVA waters blocked the surface IEX sites and reduced the adsorption of lower MW organic compounds being removed by the resin. Despite the reduced removal of DOC and UVA by SIX in this test, the treated water DOC concentration after the combined process was half that of the conventionally treated water, with DOC residuals of 0.62 and 1.25 mg/L respectively (similar to that observed in Tests 1 and 2).

The LC-OCD results show the preferences of SIX and coagulation for different organic fractions (Figure 2.2 and chromatogram traces shown in Figure 2.3). Whereas SIX preferentially removed LMW compounds, coagulation favoured the HMW compounds, which is consistent with previous work conducted using MIEX combined with coagulation for DOC removal (Humbert *et al.* 2007). The coupling of the process therefore gave much better overall removal than the single processes due to their differing selectivities for organic fractions.

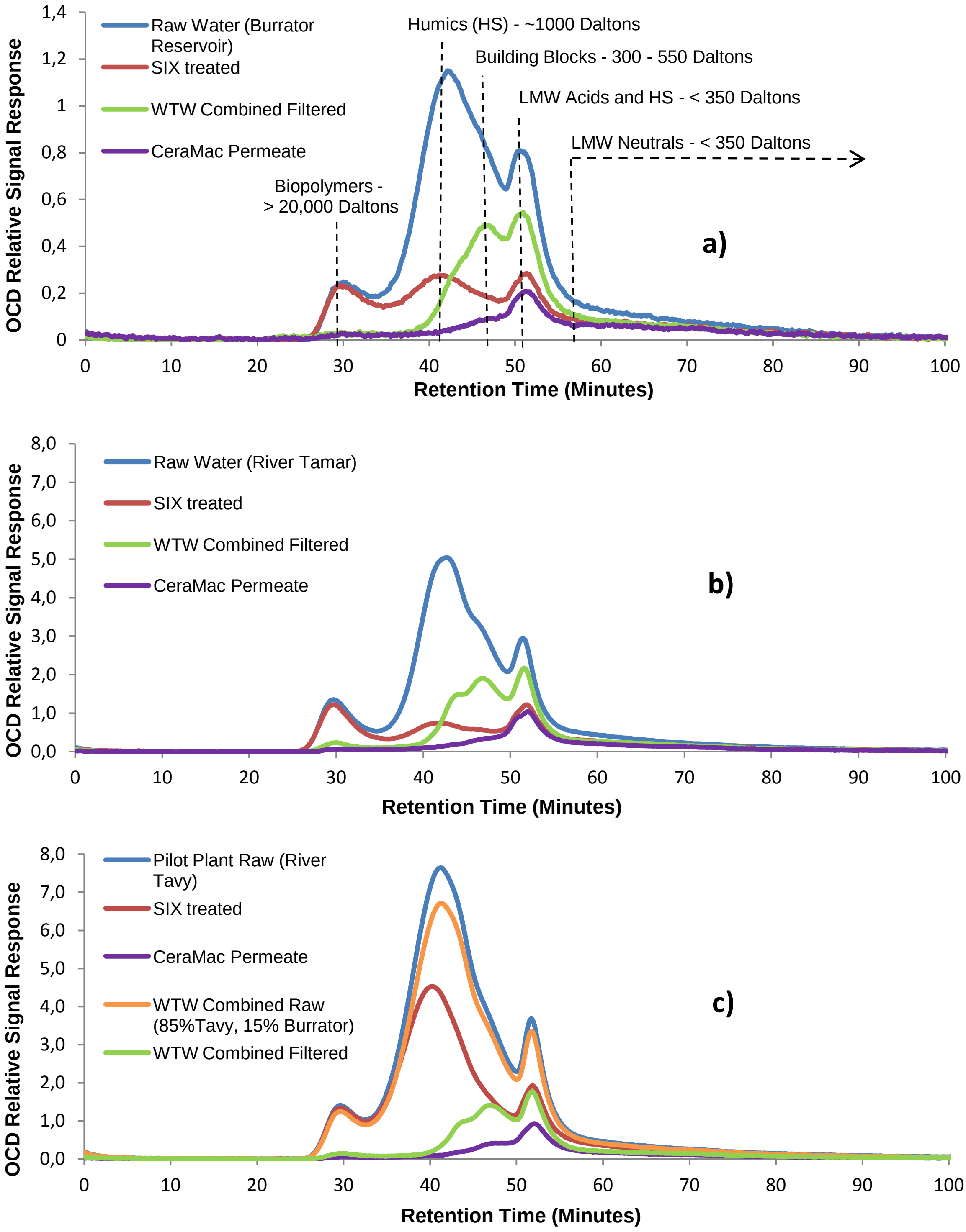

Figure 2.3. LC-OCD chromatographs, fraction removal by SIX, SIX/ILCA/CMF and conventional treatment a) Test 1 - low DOC UPRES (peak assignation and MW are shown for reference), b) Test 2 – moderate DOC LORIV and c) Test 3 – high DOC UPRIV (spate conditions). Y-axis scale expanded in a) to enable discrimination of the LC-OCD fractions/peaks.

The SIX process provided only 10-20% removal of the highest MW (>20,000 Daltons) biopolymer fraction, comprising organic colloids, polysaccharides and protein like substances. This outcome is consistent with that from other studies which have reported low removal of the highest MW organic compounds (biopolymers) by IEX (Mergen *et al.* 2009; Huber *et al.* 2011; Grefte *et al.* 2013). This is a phenomenon related to decreasing charge density with increasing MW and/or size exclusion, where the organic compounds are prevented from entering the IEX resin pores (Croué *et al.* 1999; Humbert *et al.* 2007). Some studies have, however, reported high removal of DOC from high MW fractions (Humbert *et al.* 2005; Singer *et al.* 2007; Drikas *et al.* 2011) which may relate to differences in the high MW organic characteristics (such as charge density), resin use (virgin resin) or the analytical technique used. On the latter, it should be noted that biopolymers do not usually strongly absorb UV light (Huber *et al.* 2011) and therefore are not detected by high performance size exclusion chromatography (HPSEC) using UV detection (Aslam *et al.* 2013). Coagulation was very effective at removing biopolymers (72-80%) but the combined process resulted in even greater removal of this fraction (75-95%).

Humic substances were removed more effectively by SIX (68-78% removal) than conventional treatment (65-68%) for the low to moderate DOC waters and combining the processes led to almost complete removal of this fraction for all sources (>94%). The removal of building blocks (weathering products of humic substances) by SIX (65-75%) was much greater than conventional treatment for the low to moderate DOC waters (39-46%). IEX is very effective at removing humic compounds and their breakdown products due to both groups containing similar acidic, negatively charged functional groups. Coagulation alone was less effective at removing building blocks because these compounds are more hydrophilic. LMW neutrals compounds were removed to a similar degree by SIX and conventional treatment (~35%). However, following the combined process, their removal was increased for all raw waters (35-53%) showing the clear benefits of combining SIX with coagulation. Neutral compounds have been shown to be removed by IEX through surface adsorption onto the resin surface (Cornelissen *et al*. 2008). Similarly, adsorption onto floc surfaces during conventional coagulation is likely, such that coupling the process evidently benefits removal of these fractions.

2.3.2 Disinfection by-product formation

DBPFP was investigated to assess how the improved organic compound removal from the SIX/ILCA/CMF process preferentially removed DBP precursors in comparison with conventional treatment. Overall, the removal of DBPFP by this process compares favourably when compared to previous MIEX/coagulation studies (Singer & Bilyk, 2002; Drikas *et al*. 2002; Drikas *et al*. 2003; Shorrock & Drage, 2006; Boyer & Singer, 2006; Cromphout *et al*. 2008) and recent work assessing advanced water treatment processes, including MIEX/coagulation, advanced oxidation processes and activated carbon (Bond *et al*. 2011).

The DBPFP of SIX-treated water was similar to that achieved by conventional treatment for the low and moderate DOC source waters, with THMs between 50-60 µg/L and HAAs at 60-70 µg/L in Test 1 and THMs at 100-130 µg/L and HAAs 90-100 µg/L in Test 2 (Figure 2.4). For the high DOC water (Test 3), the DBPFP of the SIX treated water was much higher due to the reduced DOC and UVA removal achieved. However, when SIX was combined with coagulation the DBPFP was very low and, as for all the waters sources investigated, much less than that achieved with coagulation alone. The combined process reduced the raw water DBPFP by 83-97% resulting in 58-67% lower THMFP and HAAFP in the treated water when compared to conventional treatment (Figure 2.4).

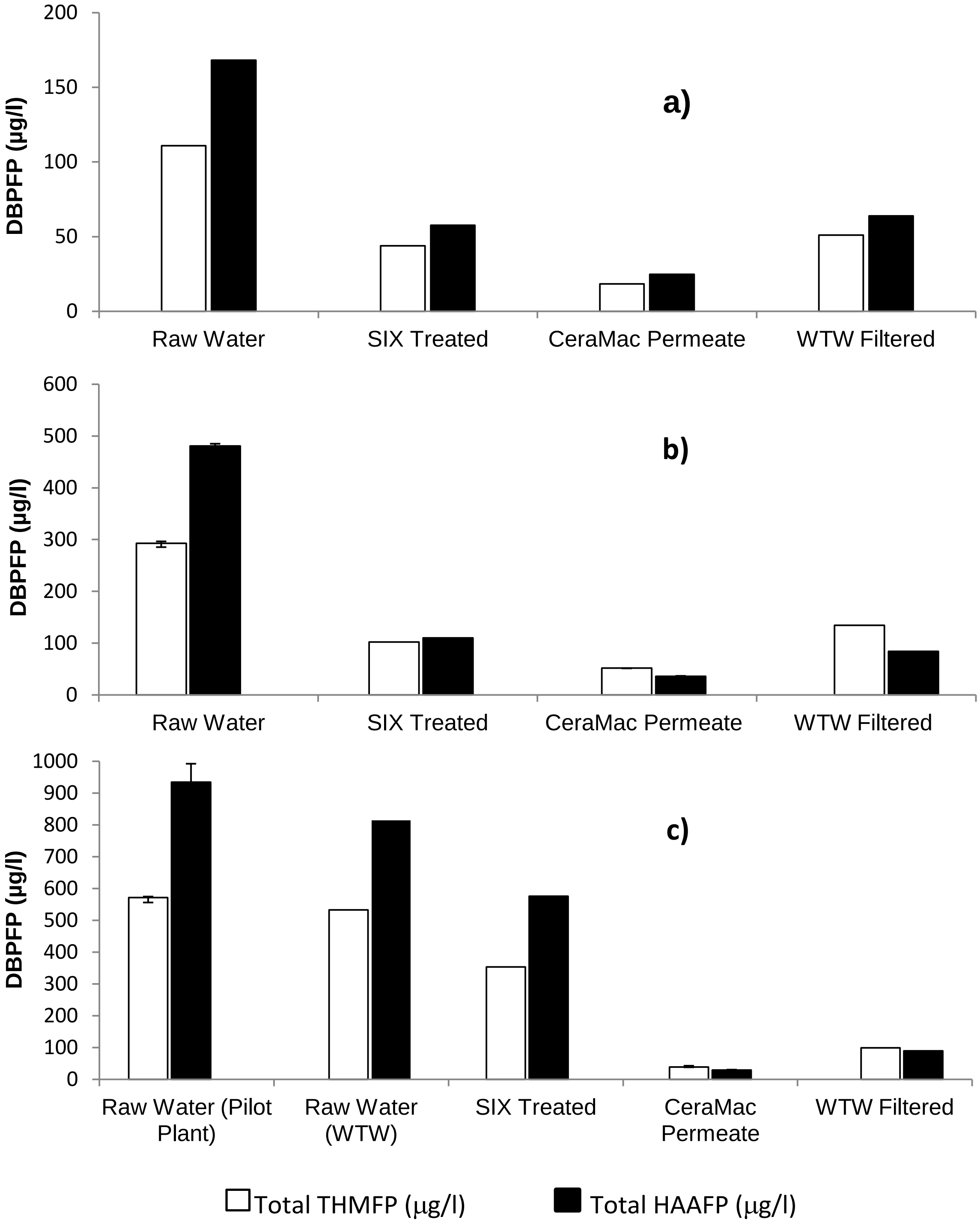

Figure 2.4. Removal of THMFP and HAAFP by SIX, SIX/ILCA/CMF and conventional treatment a) Test 1 - low DOC UPRES, b) Test 2 – moderate DOC LORIV and c) Test 3 – high DOC UPRIV. Error bars show the maximum and minimum value observed from 3 replicate samples. To enable improved clarity and comparison between processes and tests, different y-axis scales are used in a), b) and c).

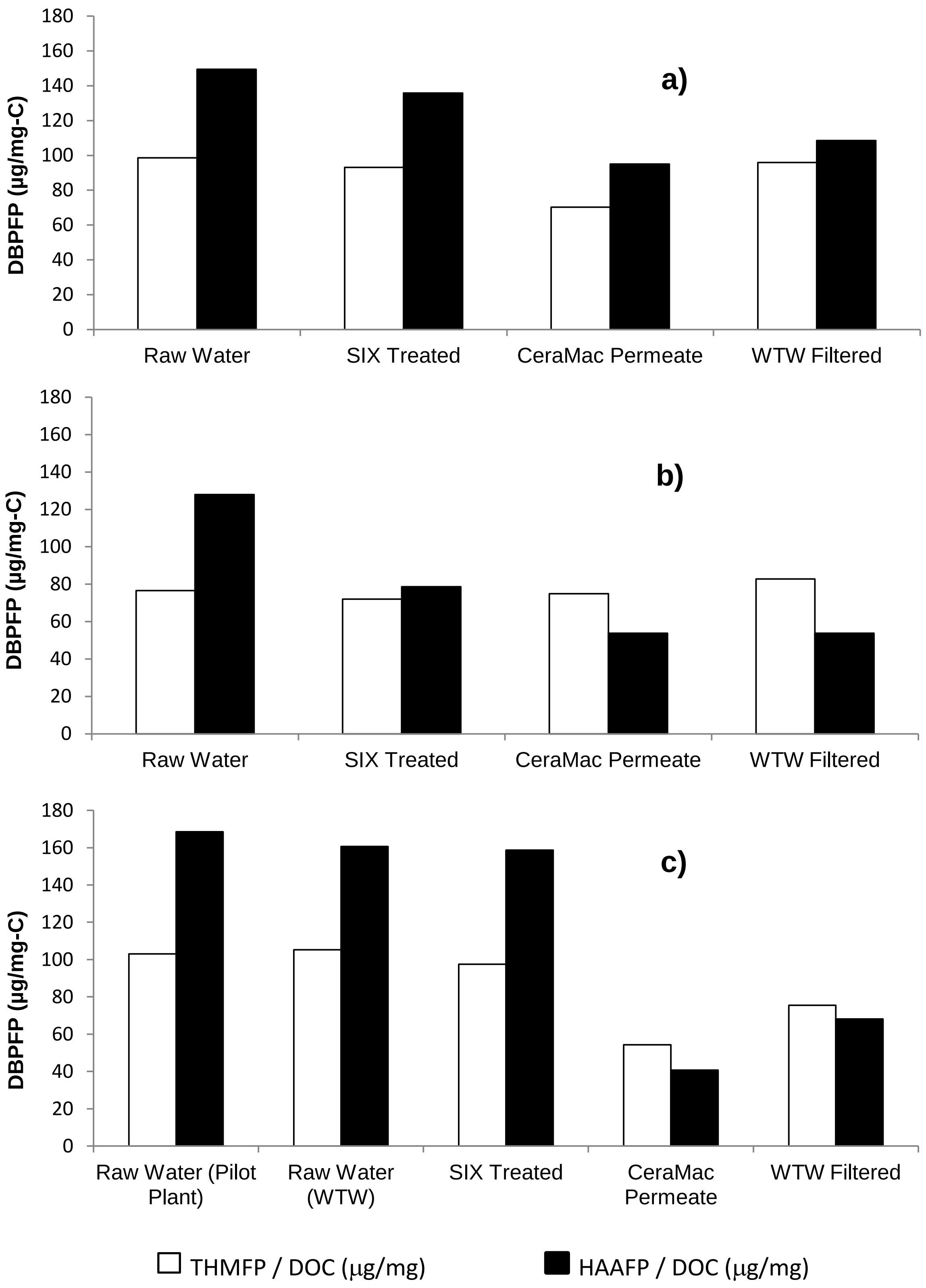

Figure 2.5. Specific THM and HAA reactivity - SIX, SIX/ILCA/CMF and conventional treatment a) Test 1 - low DOC UPRES, b) Test 2 – moderate DOC LORIV and c) Test 3 – high DOC UPRIV.

The specific reactivity (or yield) of the residual organic compounds in (µgTHMs/mgDOC) from each process was investigated to determine the extent of the impact of treatment on reactivity compared with overall DBPFP (Figure 2.5). For treatment of low and moderate DOC waters (Test 1 and 2), SIX alone led to slightly lower THM specific reactivity than conventional treatment (93 and 96 µgTHMs/mgDOC in Test 1 and 75 and 82 µg/mg in Test 2). The addition of coagulation following IEX further reduced the reactivity in the low DOC water to 70 µg/mg but the reactivity did not change in Test 2. These differences reflect the specific organic compounds found in the two water sources. For Test 1, the water was from an upland reservoir and contained relatively more hydrophobic and UV_{254} absorbing NOM than for the lowland river water. These organic compounds are very amenable to coagulation, while having a high THMFP (Liang & Singer, 2003; Bond *et al.* 2010). For water sources that contain more hydrophobic NOM, pre-treatment by IEX reduces the NOM load passing on to downstream coagulation, while not significantly changing the reactivity of the remaining organic compounds to chlorine. The probable consequence is that the reduction in NOM load enables the coagulant to remove more of the hydrophobic NOM that has a high reactivity than is the case for conventional coagulation without IEX pre-treatment. For the higher DOC water, the SIX treated water showed only a small reduction in reactivity for THM formation compared to the raw water, likely because of the high load of NOM in the water. However, the combined treatment resulted in much lower reactivity of 54 µg/mg compared to 75 µg/mg for conventional treatment.

The specific reactivity of NOM for HAA formation was reduced following IEX treatment, but the reduction following coagulation was much more significant. Coagulation significantly reduced the HAA reactivity (27-58%) in all of the waters, with the highest reductions found when treating the moderate and high DOC waters (Tests 2 and 3). These findings are consistent with the conclusions of studies which have determined that the majority of reactive HAA precursor compounds are aromatic, hydrophobic NOM. Many of these compounds are also of high molecular weight, which may exclude them from removal by IEX. However, as discussed, these compounds are very well removed by coagulation processes meaning that overall IEX followed by coagulation gave the lowest HAA reactivity levels.

A comparison of the current data with previous laboratory, pilot and full-scale studies of IEX pre-treatment (all based on MIEX) prior to coagulation, compared with conventional treatment, shows good agreement with reported data (Figure 2.6). Most of the data, including that from the current study, shows THM and HAA levels to be reduced by 40% or more compared with conventional coagulation. Reductions in HAA recorded for the IEX/coagulation process aligned with the highest of those reported, a positive result given that most of the bench scale testing has been performed using virgin resin. The DOC and UVA removal efficiency of virgin IEX resin has been shown to decrease significantly with use (Shorrock & Drage, 2006; Walker & Boyer, 2011). The resin in this study had been in continuous use for between 6 – 18 months therefore providing representative results for long term operation. In general, the reduction in DBP concentrations for the combined treatment appears to be due to improved removal of DOC and, to a lesser extent, selective removal of highly reactive organic species, with some correlation between the two. The selective removal of precursors is not always observed and is more likely when overall THM/HAA reductions are low. In the current study, all three of the conditions tested yielded reductions in THMs and in DOC reactivity; two out of three conditions revealed the same trend for HAAs. In the exceptional case, HAAs were reduced whilst the reactivity did not change.

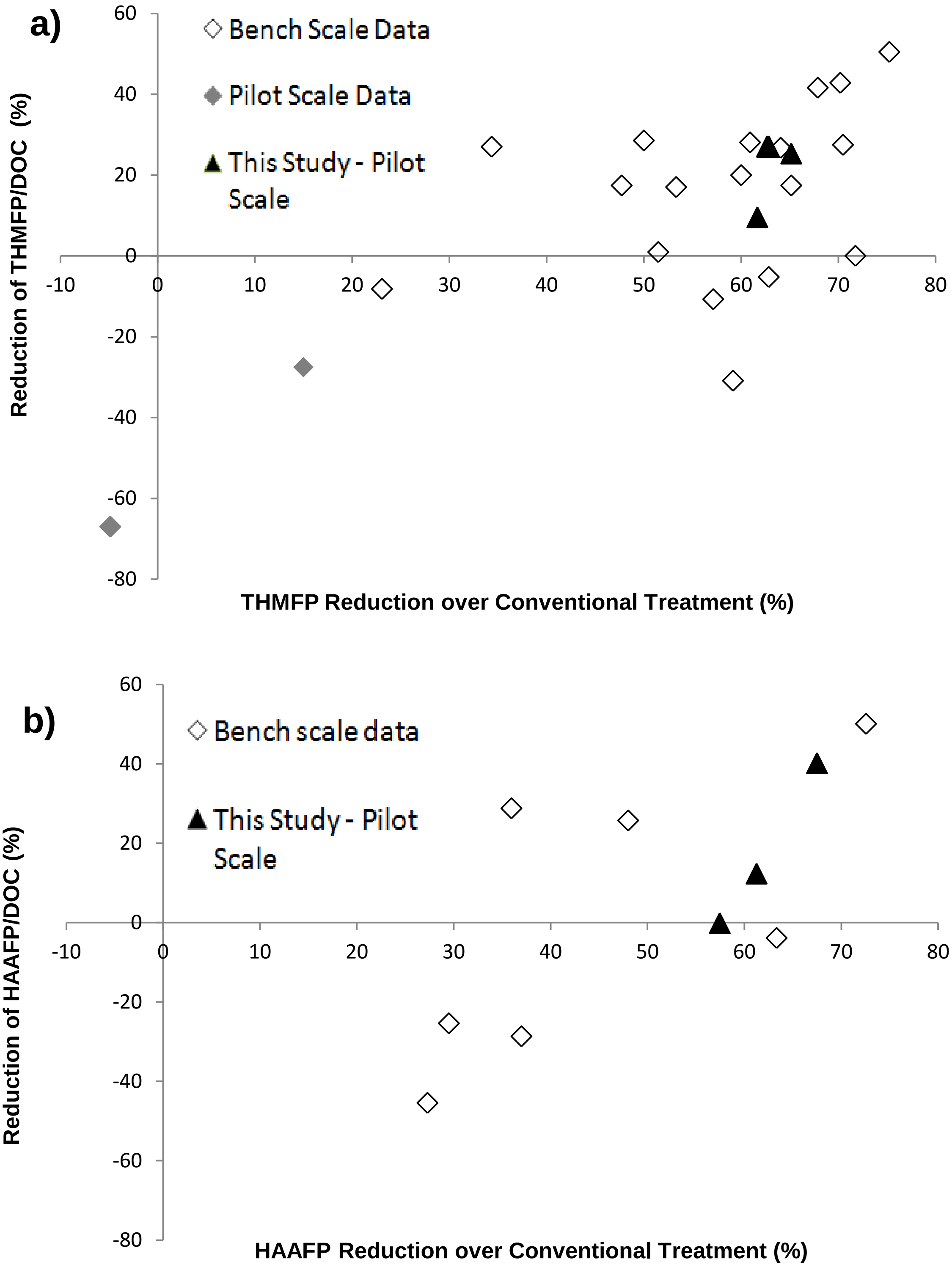

Figure 2.6. Comparison of the change in DBP concentration and reactivity by ion exchange with coagulation compared to conventional coagulation. Third party data taken from Shorrock and Drage, 2006 (pilot scale), Boyer and Singer, 2005 & 2008, Singer and Bilyk, 2002 and Drikas *et al.* 2002 &2003 (bench scale).

The LC-OCD results (Figure 2.2 & Figure 2.3) indicate that most of the additional NOM removed by the advanced process compared to conventional treatment was of low MW. Previous research has shown that these lower MW NOM fractions can contribute significantly to overall DBPFP (Kitis *et al.* 2002; Kristiana *et al.* 2010). The improved overall removal of the lower MW humic substances and building block fractions by the combined process significantly reduced the DBPFP as these more hydrophobic fractions have been shown to be the most reactive DBP precursors (Bolto *et al.* 2002; Kitis *et al.* 2002; Wassink *et al.* 2011). Improved removal of LMW neutral compounds by IEX was also observed. These compounds have previously been shown to be poorly removed by coagulation and, although generally at low concentrations, are nonetheless significant THM precursors (Hua & Reckhow, 2007). The preferential removal of LMW compounds by SIX further explains the reduced DBPs recorded for the combined process.

2.3.3 Reduction of brominated DBPs

The combined process led to apparent synergistic removal of reactive DBP precursors, which resulted in significantly reduced reactivity of the residual DOC. For example, in Test 3, when the removal of DBP precursors by SIX was reduced, the combined process lead to reductions in specific reactivity (47% for THMs and 76% for HAAs) which were higher than the sum of the removals attainable from each process individually (SIX 6% and 9%, conventional 3% and 58% for THM and HAA respectively). In addition to the removal of reactive DBP precursors, IEX can also remove bromide which, in turn, may lead to reduced concentrations of brominated DBPs (Br-DBPs) and so the specific reactivity, given that the bromide ion has a higher mass than chloride. Reduction of Br-DBPs is also important because they are thought to be more toxic than their chlorinated analogues (Singer & Bilyk 2002; Hua & Reckhow 2012). The removal of Br-DBPs was therefore further investigated to establish the removals possible with each process.

	Test 1 - UPRES			Test 2 - LORIV			Test 3 - UPRIV		
a)	Raw Water	SIX Treated	CeraMac Permeate	Raw Water	SIX Treated	CeraMac Permeate	Raw Water	SIX Treated	CeraMac Permeate
Bromide (µg/l)	29.3	15.6	15.4	63	57.2	57.3	26.1	20.1	22
HCO$_3$ Alkalinity (mg/l)	5	3	4	49	32	13	20	10	5

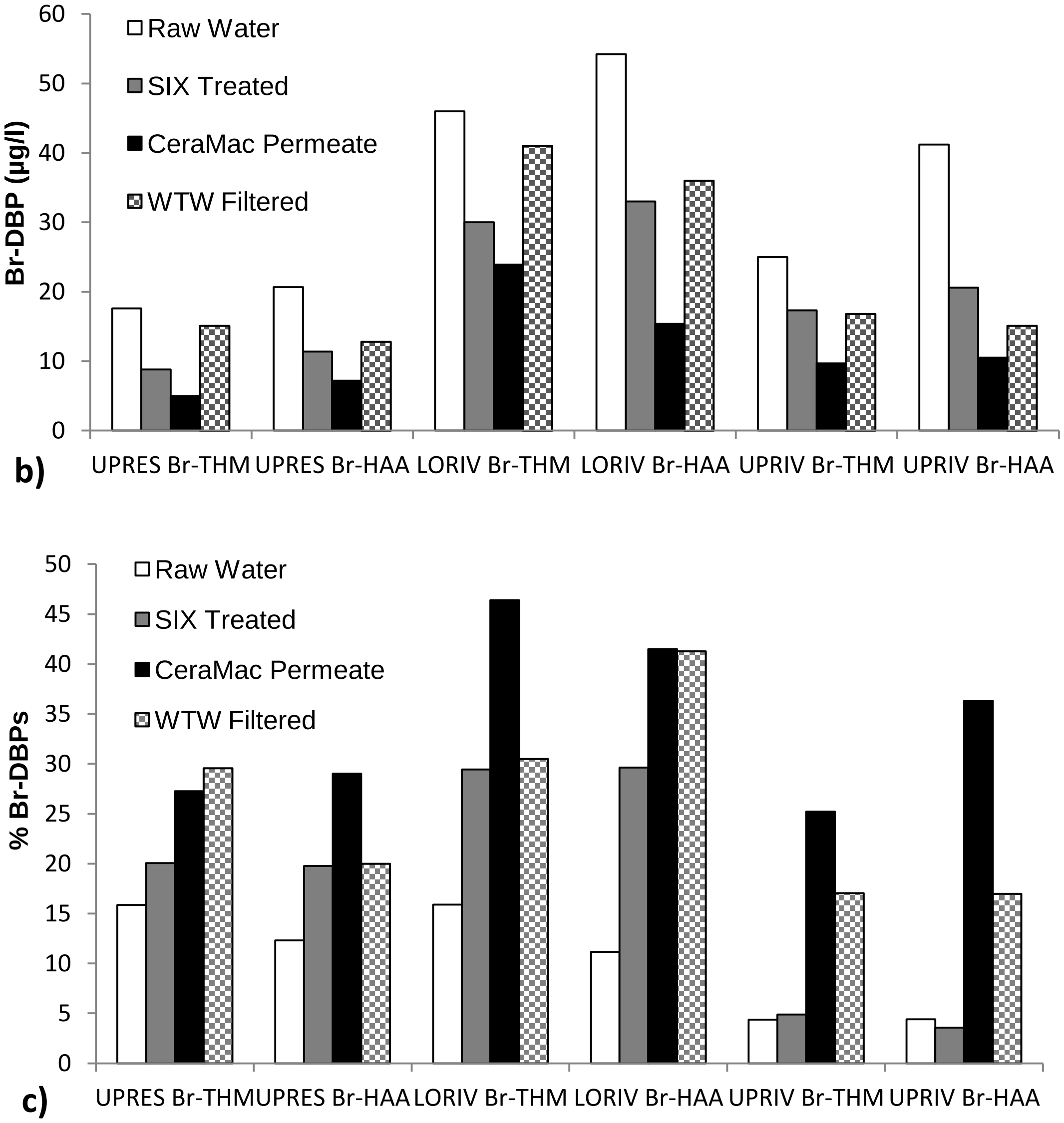

Figure 2.7. a) The relationship between bromide removal and bicarbonate alkalinity b) Br-DBP concentrations and c) % Br-DBP for Tests 1 – low DOC UPRES, Test 2 – moderate DOC LORIV and Test 3 – high DOC UPRIV.

Removal of bromide by IEX resins and subsequent reduction of Br-DBPs has been shown in previous work to be dependent upon the concentration of competing anions such as bicarbonate and sulphate (Walker & Boyer, 2011). In this study bromide removal by SIX was confirmed to be inversely related to raw water alkalinity varying between 9% for the LORIV, which had the highest alkalinity of 35 mg/L as $CaCO_3$, and 47% for the UPRES which had the lowest alkalinity at 4 mg/L as $CaCO_3$ (Figure 2.7a). As expected, and demonstrated in previous studies (Boyer & Singer, 2005; Kristiana *et al.* 2010), coagulation did not remove bromide. The concentration of Br-DBPs was lower in the SIX treated water than the conventionally treated water other than for the high DOC load in Test 3 (Figure 2.7). Br-DBP concentration was reduced significantly by SIX/ILCA/CMF, with a 48-75% reduction in comparison with the raw waters and a 30-67% reduction in comparison with the conventional process.

Despite the CMF permeate having by far the lowest concentration of Br-DBPs, these compounds represented a higher proportion of the total DBP concentration in this water (Figure 2.7c). This arises because of the very high removal of DOC provided by the combined process which leads to a reduced chlorine demand. Thus, when the removal of DOC is greater than the removal of bromide, the ratio of bromide to chlorine and DOC both increase, causing a shift towards the formation of a greater proportion of brominated THM and HAA compounds (Singer *et al.* 2007). The reductions in Br-DBP seen in water treated by coagulation are attributable to the removal of organic precursors which have a higher preference for bromine incorporation during disinfection. Previous studies reported a general trend for increased reactivity of bromine with lower MW, more hydrophilic compounds, for which the removal has been shown in the current study to be significantly higher with SIX than with coagulation (Hua & Reckhow 2012; Farré *et al.* 2013). However, Kristiana *et al.* (2010) found that the highest MW fraction (>20000 Daltons) had the highest brominated/chlorinated DBP ratio; these compounds have been shown to be much more effectively removed by coagulation than SIX in this study.

The NOM removals observed have shown that the SIX process compares favourably to existing IEX pre-treatment systems before coagulation. Although a detailed cost analysis is beyond the scope of this paper, overall capital costs for the SIX/ILCA/CMF process were similar to conventional treatment processes due to the smaller footprint and reduced associated civil and construction costs. ILCA adds very little to the capital costs since it comprises ostensibly only a tank and dosing pump. Operational cost projections are similar to conventional WTWs due to the impact of the reduced coagulant dose off-setting the supplementary costs of the pumping energy (for the membrane) and chemicals usage/disposal (for the ion exchange and membrane). The main novel feature of SIX is in the single pass nature of the ion-exchange process. This means that only freshly regenerated resin is introduced and contacted with raw water for a known period of time. This provides favourable adsorption kinetics, such that low resin inventories are needed, and reduces the opportunity for resin blinding and bio-fouling. Furthermore, IEX resins can be selected based on the characteristics of the organic compounds present in the water rather than being fixed to a particular supplier.

2.4 Conclusions

A novel combined IEX/coagulation process has been applied to the treatment of raw waters for reducing the DBPFP. The process employs suspended ion exchange (SIX) with in-line coagulation (ILCA), followed by ceramic membrane filtration. SIX and ILCA were shown to remove different organic fractions, with SIX preferentially removing the low-molecular weight fraction and coagulation removing the high molecular weight compounds. The processes were thus complimentary and when combined a broad range of organic compounds were removed resulting in very high DOC and UVA removal thus providing possible benefits in terms of the efficiency of downstream processes, improved biostability, reduced chlorine demand and better aesthetic treated water quality.

The specific reactivity of the residual organic compounds with chlorine was reduced to a greater degree by the combined process, using a reduced coagulant dose, than by either individual process. This was in part related to the SIX/ILCA/CMF process significantly reducing Br-DBP concentrations in comparison to conventional treatment. The enhanced BR-DBP removal can be attributed to reductions in bromide concentration and enhanced removal of reactive LMW organic compounds by SIX, and the removal of HMW biopolymers by coagulation. Removal of bromide by SIX was found to be strongly related to bicarbonate alkalinity. The SIX/ILCA process provided mean additional reductions in DOC, UVA, THMFP, HAAFP and Br-DBP of 50, 62, 62, 62 and 47% respectively when compared with conventional treatment which was based on coagulation and media filtration.

2.5 Acknowledgments

The authors would like to acknowledge: South West Water, Exeter, U.K who funded and supported the work and South West Water Laboratories, Exeter, U.K for the provision of water analysis; Gilbert Galjaard, Holly Shorney-Darby, Jumeng Zheng and Harry Scheerman from PWN Technologies, Netherlands for the design and build of the pilot plant and for ongoing technical support throughout the project; RWB Water Services, Almelo, Netherlands for the design, build and ongoing assistance with maintenance of the pilot plant; Het Water Laboratorium, Haarlem, Netherlands who provided LC-OCD analysis; ALS Laboratories, Wakefield, U.K for bromide and HAA analysis.

2.6 References

Allpike, B.P., Heitz, A., Joll, C.A., Kagi, R.I., Abbt-Braun, G., Frimmel, F.H., Brinkmann, T., Her, N., Amy, G., 2005. Size exclusion chromatography to characterize DOC removal in drinking water treatment. *Environmental Science and Technology*, 39 (7), pp. 2334-2342.

Aslam, Z., Dixon, M., Chow, C.W.K., Morran, J., Drikas, M., van Leeuwen, J.A., 2013. Chemometric approaches to data assessment for a long-term case study of MIEX pretreatment performance. *Desalination and Water Treatment*, 51 (16-18), pp. 3639-3649.

Bolto, B., Dixon, D., Eldridge, R., King, S., Linge, K., 2002. Removal of natural organic matter by ion exchange. *Water Research*, 36 (20), pp. 5057-5065.

Bond, T., Goslan, E, H., Parsons, S, A., Jefferson, B., 2010. Disinfection by-product formation of natural organic matter surrogates and treatment by coagulation, MIEX and nanofiltration. *Water Research,* 44, pp. 1645-1653.

Bond, T., Goslan, E, H., Parsons, S, A., Jefferson, B., 2011. Treatment of disinfection by-product precursors. *Environmental Technology*, 32 (1), pp. 1-25.

Boyer, T.H., Singer, P.C., 2005. Bench-scale testing of a magnetic ion exchange resin for removal of disinfection by-product precursors. *Water Research*, 39 (7), pp. 1265-1276.

Boyer, T.H., Singer, P.C., 2006. A pilot-scale evaluation of magnetic ion exchange treatment for removal of natural organic material and inorganic anions*. Water Research*, 40 (15), pp. 2865-2876.

Cornelissen, E.R., Beerendonk, E.F., Nederlof, M.N., van der Hoek, J.P., Wessels, L.P., 2009. Fluidized ion exchange (FIX) to control NOM fouling in ultrafiltration. *Desalination*, 236 (1-3), pp. 334-341.

Cornelissen, E.R., Moreau, N., Siegers, W.G., Abrahamse, A.J., Rietveld, L.C., Grefte, A., Dignum, M., Amy, G., Wessels, L.P., 2008. Selection of anionic exchange resins for removal of natural organic matter (NOM) fractions. *Water Research*, 42 (1-2), pp. 413-423.

Cromphout, J., Verdickt, L., Martin, E., Vanhoucke, R., Vanhullebusch, T., 2008. Comparison between magnetic ion exchange resin-ultrafiltration and enhanced coagulation-filtration for the treatment of an NOM loaded surface water. *Water Science and Technology: Water Supply*, 8 (6), pp. 643-651

Croué, J.-P., Violleau, D., Bodaire, C., Legube, B., 1999. Removal of hydrophobic and hydrophilic constituents by anion exchange resin. *Water Science and Technology*, 40 (9), pp. 207-214.

Drikas, M., Morran, J.Y., Pelekani, C., Hepplewhite, C., Bursill, D.B., 2002. Removal of natural organic matter - A fresh approach. *Water Science and Technology: Water Supply*, 2 (1), pp. 71-79

Drikas, M., Chow, C.W.K., Cook, D., 2003. The impact of recalcitrant organic character on disinfection stability, trihalomethane formation and bacterial regrowth: An evaluation of magnetic ion exchange resin (MIEX®) and alum coagulation. *Journal of Water Supply: Research and Technology - AQUA*, 52 (7), pp. 475-487.

Eaton, A, Clesceri, L, Rice, E, & Greenberg, A 2005, Standard Methods For The Examination Of Water And Wastewater. Washington, DC: American Public Health Association.

Farré, M.J., Day, S., Neale, P.A., Stalter, D., Tang, J.Y.M., Escher, B.I., 2013. Bioanalytical and chemical assessment of the disinfection by-product formation potential: Role of organic matter. *Water Research*, 47 (14), pp. 5409-5421.

Fearing, D.A., Banks, J., Guyetand, S., Eroles, C.M., Jefferson, B., Wilson, D., Hillis, P., Campbell, A.T., Parsons, S.A., 2004. Combination of ferric and MIEX® for the treatment of a humic rich water. *Water Research*, 38 (10), pp. 2551-2558.

Galjaard, G., Martijn, B., Koreman, E., Bogosh, M., Malley, J., 2011. Performance Evaluation SIX® -CeraMac® in Comparison with Conventional Pre-treatment Techniques for Surface Water Treatment. *Water Practice and Technology*, 6 (4).

Gan, X., Karanfil, T., Bekaroglu, S.S.K. Shan, J., 2014. The control of N-DBP and C-DBP precursors with MIEX. *Water Research*, 47, 1344-1352.

Grefte, A., Dignum, M., Cornelissen, E.R., Rietveld, L.C. 2013. Natural organic matter removal by ion exchange at different positions in the drinking water treatment lane. *Drinking Water Engineering and Science*, 6 (1), pp. 1-10.

Hofs, B., Ogier, J., Vries, D., Beerendonk, E.F., Cornelissen, E.R., 2011. Comparison of ceramic and polymeric membrane permeability and fouling using surface water, *Separation and Purification Technology*, Vol. 79, p 365– 374

Hua, G., Reckhow, D.A., 2012. Evaluation of bromine substitution factors of DBPs during chlorination and chloramination. *Water Research*. 46 (13), pp 4208-4216.

Huang, H., Cho, H.-H., Schwab, K.J., Jacangelo, J.G., 2012a. Effects of magnetic ion exchange pretreatment on low pressure membrane filtration of natural surface water. *Water Research*, 46 (17), pp. 5483-5490

Huang, H., Cho, H.-H., Jacangelo, J.G., Schwab, K.J., 2012b. Mechanisms of membrane fouling control by integrated magnetic ion exchange and coagulation. *Environmental Science and Technology*, 46 (19), pp 10711-10717

Huber, S.A., Balz, A., Abert, M., Pronk, W., 2011. Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography - organic carbon detection - organic nitrogen detection (LC-OCD-OND). *Water Research*, 45 (2), pp. 879-885.

Humbert, H., Gallard, H., Suty, H., Croué, J.-P., 2005. Performance of selected anion exchange resins for the treatment of a high DOC content surface water. *Water Research*, 39 (9), pp. 1699-1708.

Humbert, H., Gallard, H., Jacquemet, V., Croué, J.-P., 2007. Combination of coagulation and ion exchange for the reduction of UF fouling properties of a high DOC content surface water. *Water Research*, 41 (17), pp. 3803-3811.

Jarvis, P., Mergen, M., Banks, J., Mcintosh, B., Parsons, S.A., Jefferson, B., 2008. Pilot scale comparison of enhanced coagulation with magnetic resin plus coagulation systems. *Environmental Science and Technology*, 42 (4), pp. 1276-1282.

Kabsch-Korbutowicz, M., Urbanowska, A., 2012. Effects of ion-exchange for NOM removal in water treatment with ceramic membranes ultrafiltration. *Membrane Water Treatment*, 3 (4), pp. 211-219.

Kitis, M., Karanfil, T., Wigton, A., Kilduff, J.E., 2002. Probing reactivity of dissolved organic matter for disinfection by-product formation using XAD-8 resin adsorption and ultrafiltration fractionation. *Water Research*, 36 (15), pp. 3834-3848.

Kristiana, I., Allpike, B.P., Joll, C.A., Heitz, A., Trolio, R., 2010. Understanding the behaviour of molecular weight fractions of natural organic matter to improve water treatment processes. *Water Science and Technology: Water Supply*, 10 (1), pp. 59-68.

Lee, N., Amy, G., Croué, J.-P., Buisson, H., 2004. Identification and understanding of fouling in low-pressure membrane (MF/UF) filtration by natural organic matter (NOM). *Water Research*, 38 (20), pp. 4511-4523.

Lee, S., Cho, J., Shin, H., Son, B., Chae, S., 2003. Investigation of NOM size, structure and functionality (SSF): Impact on water treatment process with respect to disinfection by-products formation. *Journal of Water Supply: Research and Technology - AQUA*, 52 (8), pp. 555-564.

Lee, S.J., Dilaver, M., Park, P.K., Kim, J.H., 2013., Comparative analysis of fouling characteristics of ceramic and polymeric microfiltration membranes using filtration models, *Journal of Membrane Science*, Vol. 432, pp 97–105.

Mergen, M.R.D., Jefferson, B., Parsons, S.A., Jarvis, P., 2008. Magnetic ion-exchange resin treatment: Impact of water type and resin use. *Water Research*, 42 (8-9), pp. 1977-1988.

Mergen, M.R.D., Adams, B.J., Vero, G.M., Price, T.A., Parsons, S.A., Jefferson, B., Jarvis, P., 2009. Characterisation of natural organic matter (NOM) removed by magnetic ion exchange resin (MIEX® Resin) *Water Science and Technology: Water Supply*, 9 (2), pp. 199-205.

Meyn, T., Altmann, J., Leiknes, T., 2012. In-line coagulation prior to ceramic microfiltration for surface water treatment-minimisation of flocculation pre-treatment. *Desalination and Water Treatment*, 42 (1-3), pp. 163-176.

Richardson, S.D. and Ternes, T. A., 2014. Water Analysis: Emerging contaminants and current issues. *Analytical Chemistry*, 86, 2813-2848.

Shorrock, K., Drage, B., 2006. A pilot plant evaluation of the Magnetic Ion EXchange® process for the removal of dissolved organic carbon at Draycote water treatment works. *Water and Environment Journal*, 20 (2), pp. 65-70.

Singer, P.C., Bilyk, K., 2002. Enhanced coagulation using a magnetic ion exchange resin. *Water Research*, 36 (16), pp. 4009-4022.

Walker, K.M., Boyer, T.H., 2011. Long-term performance of bicarbonate-form anion exchange: Removal of dissolved organic matter and bromide from the St. Johns River, FL, USA. *Water Research*, 45 (9), pp. 2875-2886.

Wassink, J.K., Andrews, R.C., Peiris, R.H., Legge, R.L., 2011. Evaluation of fluorescence excitation-emission and LC-OCD as methods of detecting removal of NOM and DBP precursors by enhanced coagulation. *Water Science and Technology: Water Supply*, 11 (5), pp. 621-630

Watson, K., Farre, M.J. and Knight, N., 2015. Enhanced coagulation with powdered activated carbon or MIEX® secondary treatment: A comparison of disinfection by-product formation and precursor removal. *Water Research*, 68, pp. 454-466.

Zheng, D., Andrews, R.C., Andrews, S.A., Taylor-Edmonds, L., 2015. Effects of coagulation on the removal of natural organic matter, genotoxicity, and precursors to halogenated furanones (2015). *Water Research*, 70, pp. 118-129.

3 Pretreatment of surface waters for ceramic microfiltration

D. Metcalfe[1], P. Jarvis[2], C. Rockey[1], S. Judd[2,3*]

[1]South West Water, Exeter, UK.

[2]Cranfield University, Cranfield, Bedford, UK.

[3]Qatar University, Doha, Qatar.

Abstract

The influence of pre-treatment on the suppression of irreversible (IR) fouling (i.e. not recovered by the routine backwash or chemically enhanced backwashes) of ceramic membranes challenged with three UK surface waters has been studied at pilot scale. An initial scoping study compared the efficacy of suspended ion exchange (SIX) and clarification (coagulation followed by sludge blanket clarification) individually and in combination. Direct membrane filtration following in-line coagulation (ILCA) was also investigated with and without SIX. The impact on the various organic fractions, specifically high molecular weight (HMW) biopolymers (BPs) and humic substances (HSs), and lower molecular weight (LMW) building blocks (BBs) and low molecular weight neutrals (LMW-N), was studied using liquid chromatography – organic carbon detection (LC-OCD).

Results revealed SIX and coagulation to preferentially remove the LMW and high MW (HMW) organic fractions respectively. Residual HMW organic matter (primarily BPs) following SIX pre-treatment were retained by the membrane which led to rapid irreversible fouling. Coagulation pre-treatment provided stable membrane operation and the residual LMW organic compounds were not significantly retained by the membrane. Combining clarification and SIX resulted in significantly increased removal of dissolved organic carbon (DOC) and lower membrane fouling rates. Tests performed using SIX and ILCA revealed comparably high DOC removal to SIX with clarification. However, unlike the case for clarification with SIX, the addition of SIX to optimised ILCA dosing offered no additional suppression of membrane fouling compared to ILCA alone. Optimised ILCA pretreatment led to very low IR fouling rates of <0.3kPa/day trans-membrane pressure, despite highly challenging operating conditions of elevated fluxes (185 L m^{-2} h^{-1}) and highly variable feedwater dissolved organic carbon concentrations.

Keywords: Ceramic membrane; pretreatment; ion exchange; coagulation; organic fouling

3.1 Introduction

Historically, the conventional processes of coagulation, clarification and granular media filtration have been used for removing suspended material and natural organic matter (NOM) from surface water prior to disinfection (Bond *et al,* 2011). Membrane filtration offers some key advantages over such processes, including higher removal efficiency, compactness, robustness against fluctuating feed water quality, and the provision of an absolute barrier against suspended particles and pathogens such as *Cryptosporidium* (Vreeburg *et al.* 2008; Huang *et al.* 2009). Membranes have thus been increasingly applied for water treatment (Huang *et al,* 2012), with polymeric materials being most commonly used.

Recently there has been increased interest in ceramic membranes for potable and industrial water treatment applications due to their greater operational lifetime, solids loading capacity, sustainable flux rates (from reduced organic fouling), mechanical robustness and resistance to aggressive cleaning protocols (Hofs *et al.,* 2011; Lee & Kim, 2014). These and other technological benefits have meant that the higher capital costs associated with ceramic membranes can be significantly offset by lower operating costs over the life of the installation, making ceramic membranes potentially economically competitive on a whole life cost basis (Freeman & Shorney-Darby, 2011; Meyn *et al.* 2012; Shang *et al.* 2015).

Membrane fouling nonetheless remains a major obstacle to the application of membranes per se. Much research has been focussed on understanding fouling mechanisms and identifying pretreatment capable of removing highly-fouling compounds (Huang *et al.* 2009). Such research has generally revealed that the high molecular weight (HMW) biopolymer (BP) fraction of NOM is primarily responsible for irreversible (IR) membrane fouling, i.e. demanding intensive chemical cleaning in place (Fan *et al.* 2008; Tian *et al.* 2013; Kimura *et al*. 2014). Pretreatment methods which substantially remove the BP fraction have been shown to provide stable membrane operation, with coagulation being the most consistently successful method (Fabris *et al*. 2007; Humbert *et al*. 2007; Huang *et al.* 2012). Coagulation preferentially flocculates the HMW organic compounds, including BPs. The resulting solids are then either removed by clarification (e.g. sludge blanket clarification or dissolved air flotation) or, where “in-line” coagulation (ILCA) with direct filtration is used, by the backwash cycle of the membrane process.

Adsorption processes (anion exchange and activated carbon) have been shown to improve treated water quality through the removal of low molecular weight (LMW) organic compounds but, since they remove only small amounts of the high MW (HMW) fraction, in most cases fouling reduction has been shown to be minimal (Fabris *et al*. 2007; Humbert *et al.* 2007; Fan et al. 2008; Huang *et al*. 2012). Against this, some studies have revealed LMW organic molecules to cause or contribute to fouling through synergistic action with the higher MW fraction (Gray *et al.* 2011; Subhi *et al.* 2012; Lai *et al.* 2015). Such differences in findings highlight the complexity of interactions between the organic constituents and the membrane material and fouling layer.

Since coagulation and adsorption, and specifically ion exchange processes (IEX), have been shown to preferentially remove the HMW and LMW fractions of the NOM respectively, it may be surmised that their use in combination may both improve permeate water quality and suppress membrane fouling. However, previous studies of the use of combined IEX and coagulation upstream of membrane filtration have not unequivocally demonstrated membrane fouling benefits: reported fouling rates have been similar to those possible with coagulation alone (Humbert *et al*. 2007; Fan *et al.* 2008).

The current study aimed to evaluate suppression of irreversible fouling of ceramic membranes associated with pretreatment by suspended ion exchange (SIX), coagulation or a combination of both. The analysis proceeded through quantification of the organic fractions removed by both pretreatment and the membrane itself, and examined the resulting impact on membrane fouling. Experiments were conducted for three UK surface waters at large pilot scale over a 26 month period under conditions appropriate for potable water production. The irreversible fouling rate was assessed from trans-membrane pressure (TMP) transients generated under operating conditions (including physical and chemically enhanced backwashing) pertaining to those applied at full-scale.

3.2 Methods and materials

3.2.1 Raw waters

Three raw waters were tested, either individually or as a blend:

- An upland reservoir (UPRES) of low turbidity and low-to-moderate dissolved organic carbon (DOC) (Burrator Reservoir).
- A soft, upland river (UPRIV), prone to rapid changes in quality following rain, of low-to-high DOC and low-to-moderate turbidity (River Tavy).
- A lowland river (LORIV) prone to rapid changes in quality following rain of low-to-high DOC and turbidity (River Tamar).

3.2.2 Pilot plant

The 150 m^3/day pilot plant (Figure 3.1) comprised the SIX® and ceramic membrane filtration (CMF) (CeraMac®) processes and subsequently the SIX®, in-line coagulation (ILCA®) and CMF (PWN Technologies, Netherlands). These processes have been described elsewhere (Galjaard *et al*. 2011; Metcalfe *et al*. 2015) and feature:

- SIX®: an acrylic quaternary amine, gel-type strongly basic anion exchange resin in the chloride form was used throughout the trial (Lewatit S5128, Lanxess, Germany). The resin was generally dosed at 18 ml/L with a contact time of 30 min, with dosing conditions informed by preliminary bench-scale tests. Tests were also performed with lower or zero resin doses (i.e. with ILCA® only) as appropriate. The resin was in continuous use over the 2 years of the trial.
- A Lamella separator was used for separating the resin from the treated flow and the resin regenerated with 30 g/L NaCl. SIX-treated water samples were collected directly after resin separation.
- ILCA® using polyaluminium chloride (WAC®, Water Treatment Solutions, UK, 0.53-4.23 mg/L as Al) was used alone or following SIX pretreatment. Water was pH-corrected with NaOH or HCl (Brenntag, U.K), injected with coagulant, and mixed by a static mixer and flocculated for 2.4-3.9 minutes prior to CMF (direct filtration). The coagulation pH was circa 6.4 for all tests.
- CMF was carried out using a vertically mounted 25 m^2 ceramic membrane element (Metawater, Japan, nominal pore size 0.1 mm) operating by dead end filtration.

3.2.3 Full scale WTWs process

The water treatment works ((WTWs) Crownhill WTWs, South West Water (SWW), Plymouth, U.K) treated water using optimised coagulation with aluminium sulphate dosed at 3.39-6.36mg/L as Al (Kemira, U.K) and Magnafloc LT25 (BASF, U.K) anionic polyelectrolyte at 0.1-0.2 mg/L. Powdered activated carbon (PAC, Aquasorb BP2, Jacobi, U.K) was dosed at 2-3 mg/L prior to coagulation. The WTWs coagulant dose was optimised through jar testing and works operation. Clarified water following flash mixing, flocculation and solids-liquid separation (by sludge blanket clarification) was supplied to the pilot plant for some of the tests.

3.2.4 Pretreatment

The pilot plant was fed with either raw or, during the clarification or clarification + SIX campaigns, clarified water (Figure 3.1).

Tested pretreatment options for CMF comprised:

1) Clarification only, or clarification followed by SIX: Raw water was treated by the full scale clarification process and the water piped from the clarifier outlets to the pilot plant feed tank. During clarification-only tests the SIX process was taken off-line and all resin was removed. Additional tests were performed where the clarified water was further treated by SIX within the pilot plant, prior to CMF.
2) SIX followed by ILCA, or ILCA alone: ILCA was employed following the SIX process, or when ILCA was used alone the SIX process was taken off line and the resin was removed. For most tests the coagulant dose and pH correction was manually controlled, which led to periods of sub-optimal operation due to the rapidly changing raw water sources. The pH and coagulant dosing systems were automated in March 2015.

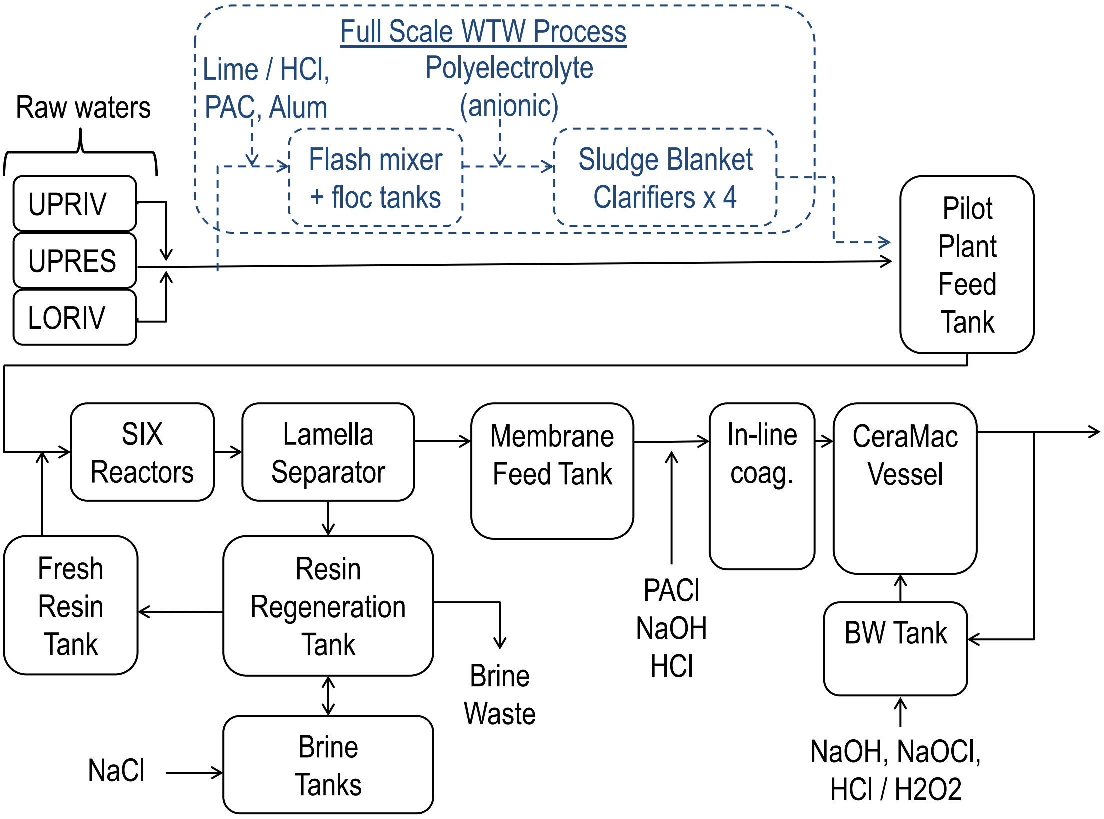

Figure 3.1 Process Flow Diagram

3.2.5 Ceramic microfiltration (CMF)

The CMF membrane flux was varied between 109 and 250 LMH (L/(m^2h)). A new membrane was installed at the start of the trials in March 2013, replaced by a new element after 2 years in operation (March 2015) prior to extended tests with automated coagulant and pH control.

Backwashing and chemically enhanced backwashing (BW and CEB) were performed following a given filtration load, measured in litres of feed solution filtered per m^2 membrane surface (L/m^2). BW used 75 L permeate pressurised to 5 bar (reduced to 4 Bar during ILCA or SIX / ILCA tests) and passed through the membrane in a reverse flow direction. CEBs with NaOCl (100 mg/L), NaOH (pH 12) or acid + H_2O_2 (pH 2.5, 100 mg/L H_2O_2) were performed at 2 bar pressure. The membrane was soaked in the reagent for 10 minutes prior to a standard BW. BW or CEB was followed by an air flush of the membrane feed channels at 2 Bar air pressure. Process conditions for the tests are reported in Table 3.1.

After each discrete test, cleaning in place (CIP) was performed by circulating chemical solution through the membrane for an extended period of time (3 – 24 hours). Generally an overnight CIP using NaOH (pH 12-12.5) was performed, followed by a CIP with either NaOCl (100-500 mg/L) or HCl/H_2O_2 (pH 2.7, 100 mg/L H_2O_2) if required to increase the specific flux to >300 LMH/Bar at 10°C prior to starting a new test. This low specific flux target (300 LMH/Bar at 10°C) did not constitute an optimised recovery of permeability but provided an attainable standard permeability for each test, despite the significant fouling which occurred in some of the scoping trials. Following the final extended tests, based on a virgin membrane with automated coagulant and pH control, an intensive CIP was performed which fully recovered membrane permeability (to ~1250 LMH/bar at 10°C). The conditions for the intensive CIP were 30 minutes at pH 2.7 with 100mg/l H2O2, followed by 1 hour at pH 12 (NaOH), followed by 2% NaOCl for 3 days.

Table 3.1 Test Process Conditions ***Backwash (BW) and chemically enhanced backwash (CEB) sequences have been described as, for example, (5 BW, NaOCl CEB) x 4, 5 BW, HCl/H2O2 CEB – this would denote 5 BW followed by a NaOCl CEB with this sequence being repeated 4 times. Following this 5 BW and then an HCl/H2O2 CEB would occur and then the entire sequence would be repeated.**

Test No.	*Raw water source*	*Pretreatment*	*Flux (LMH)*	*Filtration load prior to BW / CEB (L/m^2)*	*BW number prior to CEB / CEB sequence and chemicals**	*Water recovery (%)*
1	UPRES	SIX	150	75 / 450	(5 BW, NaOCl CEB) x 4, 5 BW, HCl/H_2O_2 CEB	95.3
2	UPRES	SIX	150	75 / 450	(5 BW, NaOCl CEB) x 4, 5 BW, HCl/H_2O_2 CEB	95.3
3	UPRIV / UPRES	Clarification only	150	75 / 450	(5 BW, NaOCl CEB) x 4, 5 BW, HCl/H_2O_2 CEB	95.3
4	LORIV/UPRIV/UPRES	Clarification / SIX	150	75 / 450	(5 BW, NaOCl CEB) x 4, 5 BW, HCl/H_2O_2 CEB	95.3
5	UPRES	SIX + ILCA	185	100 / 1800	17BW, NaOH CEB, HCl/H_2O_2 CEB	96.8
6	UPRES	SIX + ILCA	185	100 / 1800	17BW, NaOH CEB, HCl/H_2O_2 CEB	96.8
6a	UPRES	SIX + ILCA	185	100 / 1800	17BW, NaOH CEB, HCl/H_2O_2 CEB	96.8
7	UPRIV	SIX + ILCA	185	100 / 1800	17BW, NaOH CEB, HCl/H_2O_2 CEB	96.8
8	LORIV	SIX + ILCA	185	100 / 1800	17BW, NaOH CEB, HCl/H_2O_2 CEB	96.8
9	UPRES	ILCA Only	109	150 / 1800	(17BW, NaOH) x 3, 17 BW, NaOH CEB, HCl/H_2O_2 CEB	97.8
10	UPRES	9ml/l SIX + ILCA	109	150 / 1800	(17BW, NaOH) x 3, 17 BW, NaOH CEB, HCl/H_2O_2 CEB	97.8
11	UPRES	18ml/l SIX + ILCA	109	150 / 1800	(17BW, NaOH) x 3, 17 BW, NaOH CEB, HCl/H_2O_2 CEB	97.8
12	UPRES	ILCA Only	109	150 / 1800	(17BW, NaOH) x 3, 17 BW, NaOH CEB, HCl/H_2O_2 CEB	97.8
13	UPRES	18ml/l SIX Only	109	150 / 1800	(17BW, NaOH) x 3, 17 BW, NaOH CEB, HCl/H_2O_2 CEB	97.8

3.2.6 Coagulant dose optimisation

20 jar tests were performed on a wide range of raw or SIX treated waters from each of the 3 sources to establish a means of optimising the coagulant dose for minimising membrane fouling. The data from these jar tests revealed an excellent correlation ($R^2 = 0.96$) between the optimum coagulant dose and feed water filtered UV transmittance (UVT) (Figure 3.2), the optimum coagulant dose determined as being the minimum coagulant dose in mg/L as Al providing maximum achievable UVT removal.

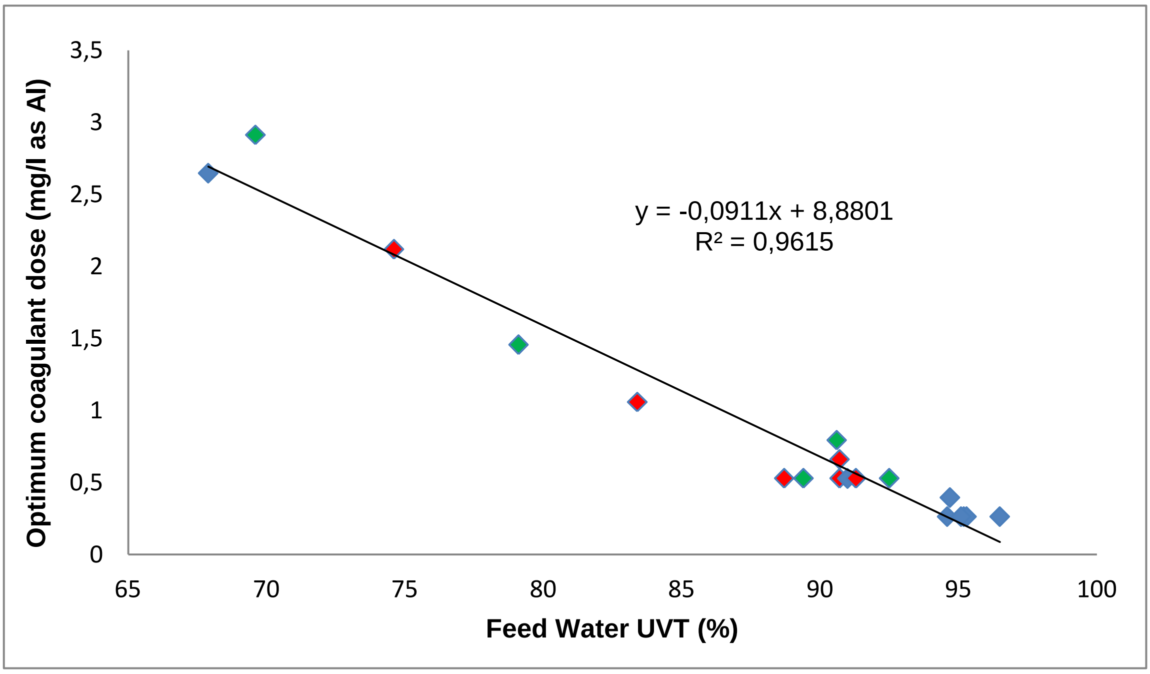

Figure 3.2 Feed water UVT vs. optimum coagulant dose jar test results. Red = UPRES, blue = UPRIV, green = LORIV

Applications of this dose resulted in negligible membrane adsorption of DOC according to liquid chromatography-organic carbon detection (LC-OCD) analysis and on-site membrane feed and permeate UVT measurements (Section 2.9). Most of the tests were conducted with daily manual adjustments to the coagulant dosing, based on the feed water UVT according to Equation 3-1, along with pH correction. This resulted in occasional sub-optimal coagulation conditions when rapid changes in raw water quality took place, subsequently leading to increased membrane fouling.

$$C_{opt} = 8.88 - 0.0911*UVT_{feed} \qquad \textbf{Equation (3-1)}$$

3.2.7 Automated coagulant dosing and pH correction

In March 2015 automated coagulant and pH control was installed. A Spectro::lyser (S::CAN, Austria) was used to measure the solids-compensated UVT of the water in the membrane feed tank, for which measured values were similar to manual filtered UVT samples. A controller used the on-line UVT_{feed} value with Equation 3-1 to provide the required coagulant dose. pH control was automated to control to a set-point of 6.4 via a negative feedback loop/controller.

3.2.8 Membrane fouling rate

Irreversible membrane fouling (i.e. not recovered by the routine BW and CEB) was measured so as to determine the required CIP frequency during full-scale operation. Individual filtration runs were generally based on a total filtration volume of 625 m^3, the filtration run time then varying with flux. An extended run was performed with a virgin membrane, with automated coagulant and pH control. TMP and temperature data (logged at one minute intervals) from each test was analysed. TMP data following CEBs were selected and the values corrected to 10°C. The fouling rate in kPa/day was determined by linear regression, with the corresponding R^2 value (Table 3.2).

3.2.9 Sample analysis

Turbidity was analysed using a Hach Lange 2100AN Turbidimeter (Hach Lange, Germany). 0.45 µm-filtered UV transmittance (UVT) was measured using a Hach DR6000 spectrophotometer (Hach Lange, Germany). DOC was characterised by LC-OCD analysis at Het Water Laboratorium (Netherlands), which quantified concentrations of total DOC and the discrete MW fractions of biopolymers (BPs), humic substances (HSs), building blocks (BBs), LMW neutrals (LMW-Ns) and LMW acids (Huber *et al*., 2011). LMW acids were not detected by LC-OCD analysis since organics within this band (50 minute elution time, equating to <350 Daltons) absorbed no UV and were hence classified by the analysis/software as LMW-HS. Turbidity and LC-OCD results for each test are reported in Table 3.2.

Adsorption of DOC and the fractions thereof onto the membrane was assessed through concentration difference between the feed and permeate. Since UVT was found to correlate reasonably well (R^2 = 0.63-0.92) with DOC concentration, all source water organic fractions being strongly UV absorbing, UVT data were used to derive organic carbon values in those tests where no LC-OCD data was collected.

3.3 Results

3.3.1 Scoping studies SIX, clarification or clarification + SIX (Tests 1-4)

A number of initial tests (Tests 1-4, Table 3.1 & Table 3.2) were performed to establish the influence of pre-treatment on irreversible fouling. These tests compared SIX treatment alone, at pilot scale, with a full scale clarification process and a combined process where the clarified water was further treated by SIX, at 150 LMH. LC-OCD analysis illustrated clear differences in the organic fractions removed by SIX, clarification and a combined process of clarification followed by SIX (Figure 3.3 a-d). SIX pre-treatment preferentially removed LMW organic compounds whilst the removal of HMW fractions by SIX was low, especially for the highest MW BP fraction (25-29%). Conversely, coagulation pretreatment preferentially removed the highest MW fractions (particularly BP) whilst the LMW organic fractions were removed to a lesser extent than possible with SIX (especially lower MW HS and BB fractions) (Figure 3.3c). These data are consistent with the findings of previous studies showing some LMW NOM to be recalcitrant to coagulation and the removal of high MW BPs by IEX to be marginal (Fabris *et al.* 2007; Humbert *et al.* 2007; Mergen *et al.* 2009; Huber *et al.* 2011; Myat *et al.* 2012). Subsequently, clarification followed by SIX was found to yield very low residual DOC concentrations (Figure 3.3d), in keeping with previously reported findings (Singer & Bilyk, 2002; Fearing *et al.* 2004; Humbert *et al.* 2007; Fan *et al.* 2008; Jarvis *et al.* 2008).

In Tests 1 and 2, following SIX pre-treatment, the majority (58-80%) of the residual HMW organic compounds were retained by the membrane (Figs. 3a and b). At the lowest DOC levels (Table 3.2, Test 1 and Figure 3.3a), a low-to-moderate fouling rate of 3.6 kPa/day was obtained at 150 LMH. When DOC increased for the UPRES source and an organic compositional change occurred resulting in a near three-fold increase in the concentration of the HMW BP fraction, a very high membrane fouling rate (48 kPa/day) was recorded (Table 3.2, Test 2 and Figure 3.3b). Further tests with SIX pre-treatment were performed on higher DOC reservoir and river water sources (UPRES, UPRIV and LORIV) at 100 and 150 LMH. Despite reductions in filtration volume prior to backwash and CEB, all of these tests yielded very high fouling rates (82-863 kPa/day).

Table 3.2 Test membrane irreversible fouling rates and water quality data

Test No.	Irreversible (IR) fouling Rate (kPa/day)	IR fouling R^2 value	Filtration time (days)	Water Source	Turbidity (NTU)	LC-OCD data						
						TOC (µg/l)	DOC (µg/l)	CDOC (µg/l)	BP (µg/l)	HS (µg/l)	BB (µg/l)	LMW-N (µg/l)
1	3.6	0.86	5.88	Raw	0.58	1863	1751	1668	143	1003	269	254
				SIX	0.75	727	677	565	107	243	82	134
				CMF	0.10	552	540	454	45	214	75	120
2	47.7	0.90	1.74 [S]	Raw	2.10	2529	2372	2372	402	1276	356	338
				SIX	1.80	1080	1023	1020	287	409	114	210
				CMF	<0.1	642	603	547	55	223	101	168
3	6.2	0.97	5.33	Raw	2.00	3974	3801	3538	232	2429	458	419
				Clarified	0.99	994	937	924	51	351	291	231
				CMF	<0.1	973	936	826	35	342	262	187
4	0.7	0.87	5.47	Raw	1.70	1863	1786	1677	272	855	303	248
				Clarified	0.33	843	738	659	47	359	87	167
				C+S	0.42	492	459	377	43	52	170	113
				CMF	0.29	473	441	358	37	43	146	132
5	6.1	0.99	5.91	Raw	0.57	2288	2273	2297	124	1606	284	282
				SIX	0.60	1516	1519	1440	113	935	154	238
				ILCA	0.86	401	303	371	21	41	144	165
				CMF	<0.1	364	311	346	32	46	121	147
6	5.4	0.96	3.92 *WQ	Raw	0.69	2060	1917	1976	188	1194	303	290
				SIX	0.8	922	883	773	161	323	116	172
				ILCA	1.4	563	425	356	30	47	161	119
				CMF	0.1	479	466	356	41	51	147	116
6a	571.4	1 (2 data points)	0.27 *S	Raw	NS	5188	5028	5248	365	3733	572	578
				SIX	NS	2742	2667	2810	321	1774	312	402
				ILCA	NS	2809	2560	2816	378	1679	297	460
				CMF	NS	951	906	835	71	408	148	208
7	10.6	0.86	3.94*WQ	Raw	1.20	1524	1402	1484	274	740	239	232
				SIX	1.40	747	642	661	220	223	91	127
				ILCA	1.30	374	334	356	52	46	137	121
				CMF	<0.1	393	331	316	44	45	116	111
8	3.8	0.95	5.37	Raw	5.30	4150	4011	4279	443	2683	605	548
				SIX	5.50	1665	1555	1572	379	651	212	330
				ILCA	5.90	1034	850	803	47	149	323	282
				CMF	0.13	966	855	777	40	148	313	276
9	2.1	0.83	5.6	Raw	1.10	2890	2635	2623	181	1861	292	289
				ILCA	1.00	771	741	600	40	220	176	164
				CMF	0.31	707	645	520	27	161	182	150
10	1.7	0.94	5.6	Raw	0.96	2787	2630	2592	184	1828	308	272
				SIX	1.00	2283	2117	2022	155	1370	274	223
				ILCA	1.60	599	471	433	35	139	126	133
				CMF	<0.1	503	485	392	31	114	124	123
11	1.7	0.93	5.6	Raw	0.74	2334	2245	2136	132	1452	297	254
				SIX	0.78	1812	1788	1660	121	1083	228	228
				ILCA	1.40	523	512	441	30	156	110	143
				CMF	0.17	471	435	359	25	114	96	123
12	1.4	0.93	5.6	Raw	0.65	2187	2129	2040	119	1404	258	259
				ILCA	0.72	717	688	609	29	229	163	187
				CMF	0.11	550	512	458	26	139	147	147
13	Very high fouling - max TMP caused shutdown			Raw	0.87		*2360*					
				SIX	1.05		*1100*					
				CMF	0.14		*850*					

[S] run stopped due to shut-down; WQ water quality change, NS not sampled, NTU nephelometric turbidity units, TOC total organic carbon, DOC dissolved organic carbon, CDOC chromatographically detectable DOC, BP biopolymers, HS humic substances, BB building blocks, LMW-N low molecular weight neutral. Italicised DOC values (Test 13) were inferred from UVT data. Test 6a shows the fouling rate under suboptimal coagulation conditions prior to shutdown.

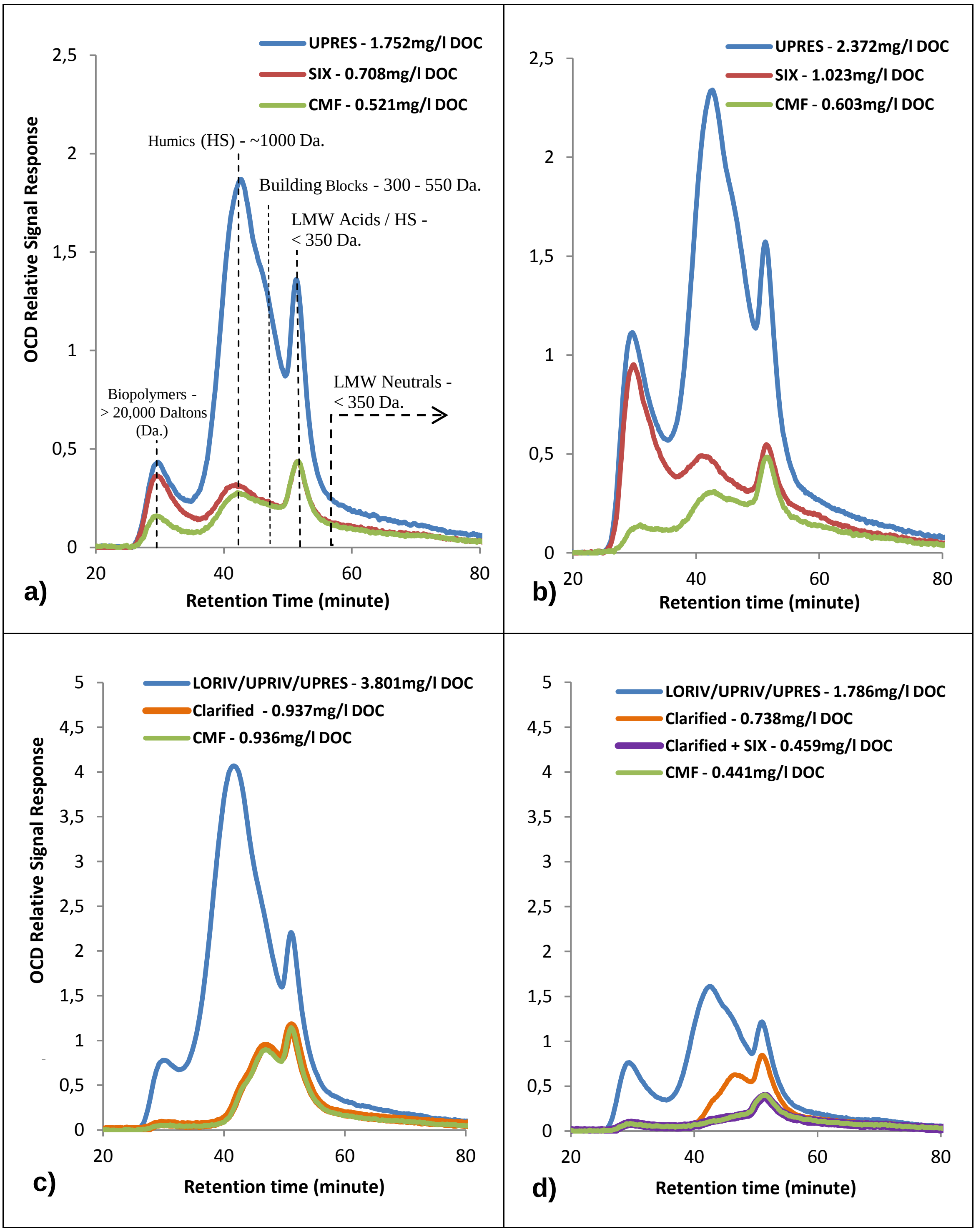

Figure 3.3 LC-OCD chromatograms for SIX, clarification and clarification & SIX pretreatments for CMF a) Test 1: SIX only with low DOC UPRES raw water (fraction peak assignation shown for reference), b) Test 2: SIX only with moderate DOC UPRES raw water, c) Test 3 – Clarification only with moderate DOC blend of raw waters, d) Test 4 – Clarification followed by SIX with low DOC blend of raw waters

For the lowest raw water organic concentrations (e.g. Table 3.2 - Test 1), fouling was effectively abated by the routine physical and chemical cleaning. The increased fouling recorded in Test 2 was associated with greater retention of HMW organic fractions than for Test 1 (80% vs. 58% for BP), corroborating previous work on the deleterious impact of increasing BP mass loads on irreversible fouling (Fabris *et al*. 2007; Fan *et al*. 2008; Zheng *et al*. 2010; Huang *et al*. 2012; Myat *et al.* 2013; Tian *et al.* 2013; Kimura *et al.* 2014; Shang *et al.* 2015). Whilst ion exchange can significantly reduce overall DOC concentrations, previous research indicates that it does not lead to significant reductions in membrane fouling due to the limited removal of the HMW NOM (Fabris *et al*. 2007; Humbert *et al.* 2007; Fan *et al*. 2008; Huang *et al*. 2012). Analysis of the adsorbed organic fractions revealed that a good correlation was obtained between membrane fouling and adsorption of (a) overall DOC (R^2 = 0.89), (b) BPs (R^2 = 0.95) and (c) HSs (R^2 = 0.98), whereas the correlations with LMW fractions were significantly weaker (R^2 = 0.14-0.33).

Test 3, using fully clarified water from the full-scale plant (Figure 3.3c), was performed under the same membrane operating conditions as Tests 1 and 2 (using SIX pretreatment) but whilst challenged with more highly fouling river water. Results showed that the removal of the HMW organic fractions by clarification provided a low-to-moderate fouling rate of 6.2 kPa/day (Table 3.2, Test 3). Whilst pre-clarification removed the LMW organic compounds to a lesser extent than possible with SIX pretreatment (Figure 3.3c), these compounds were not retained by the membrane whereas the HMW NOM was largely retained following SIX pretreatment. Following coagulation pretreatment no adsorption was detected. In Test 4 the clarified water was further treated by SIX (under the same operational conditions as Tests 1-3) to establish if removing additional LMW organic compounds from the clarified water, would further suppress membrane fouling. The lower fouling rate of 0.9 kPa/day (Table 3.2, Test 4) was associated with negligible DOC adsorption (0.018 mg/l DOC. Figure 3.3d), although the apparent adsorption recorded was higher than in Test 3.

Further tests comparing clarification only with clarification + SIX using the same operational conditions as Tests 1-4 at a higher applied flux of 175 LMH, indicated a moderate fouling rate of 11 kPa/day for clarification alone and a much lower rate of 2.4 kPa/day for clarification + SIX, despite a significantly higher raw water DOC. As with Test 3 and 4, DOC adsorption was negligible (-0.022 vs. 0.037 mg/L for clarification vs. clarification + SIX). This suggests when fouling was low, the fouling was related to factors other than organic adsorption, such as floc characteristics (Jarvis *et al*. 2008). It is also possible that the ion exchange material adsorbs any residual anionic polyelectrolyte from the clarification process, which would otherwise affect membrane fouling (Wang *et al.* 2011; Yu *et al.* 2013). Two further tests with clarification + SIX pre-treatment performed with the same operational conditions as Tests 1-4 but at higher fluxes of 200 and 250 LMH, yielded fouling rates of 5.5 and 197 kPa/day respectively, suggesting that the highest value exceeded the critical flux.

3.3.2 SIX/ILCA pre-treatment with enhanced CEB, manual control (Tests 5-8)

Jar tests confirmed that contact times below two minutes were sufficient for flocculating residual HMW organic compounds following SIX treatment of the three raw waters, corroborating work performed by Meyn *et al.* (2012) on ILCA upstream of membrane filtration. Subsequent pilot trials were conducted with SIX followed by pH correction and 2-4 minutes ILCA at relatively low coagulant doses (50-90% less than that employed for the full-scale clarification process), permitted by the removal of a large amount of DOC by SIX (Humbert *et al*. 2007; Jarvis *et al.* 2008; Huang *et al*. 2012). A flux of 185 LMH was employed for these trials, with a NaOH-based CEB: supplementary trials revealed NaOH to be more effective than NaOCl for CEB.

Analysis of the organic content of the three raw water types used for these tests revealed it to be dominated by aromatic organic compounds (high SUVA) with all organic fractions, including BPs, adsorbing UV strongly. The UVT could thus be used as a relatively accurate surrogate measure of DOC, confirmed by the strong correlation (R^2 = 0.92) between UVT and the LC-OCD-determined DOC.

The algorithm from jar test data (Equation 3-1) was used to manually set the coagulant dose based on the feed water UVT. This generally led to negligible adsorption of organic matter on the membrane and corresponding low fouling rates. High observed membrane fouling, following rapid changes in raw water quality and subsequent sub-optimal coagulation conditions, was accompanied by measurable organic compound adsorption.

Results from Tests 5-8 (Table 3.2) indicated that for optimised, manually-controlled coagulant dosing and pH adjustment, membrane fouling was low to moderate (3.8–11 kPa/day) at the high flux of 185 LMH. The DOC removal by the SIX ILCA CMF process was similar to that attained in the scoping trials based on full-scale clarification followed by SIX, i.e. 74-88% relative to the raw water. As with the scoping trials with clarification alone and clarification + SIX (Table 3.1 & Table 3.2, Tests 3 & 4), changes in fouling rate could not be related to the LC-OCD data as membrane organic adsorption was negligible when coagulation conditions were optimised. Further tests with the same operational conditions as Tests 5-8, but at a lower flux of 112 LMH yielded low fouling rates of 1.0-1.7 kPa/day. Instances of non-optimum coagulation conditions, due to rapid changes in raw water quality, always led to rapid fouling which was reflected by measurable organic compound adsorption onto the membrane (Table 3.2, Test 6a). These results demonstrate the critical nature of optimal pre-coagulation in direct membrane filtration.

3.3.3 IEX dose trials in combination with ILCA (Tests 9-13)

Tests conducted at 109 LMH on standard, reduced or zero SIX pretreatment yielded low fouling rates of 1.4-2.1 kPa/day at doses of 0 to 18 ml/L SIX (Table 3.1 & Table 3.2, Tests 9-12), with optimised coagulant dosing. Coagulant demand increased with decreasing SIX dose, but under these optimised coagulation conditions there was no correlation between fouling and SIX dose with the fouling rate remaining stable at 0, 9 or 18g/l resin doses. However, when the ILCA was taken off line and SIX pretreatment alone was employed, rapid fouling was observed (Table 3.1 & Table 3.2, Test 13). This confirmed the relative importance to membrane fouling of enmeshment of HMW BP within coagulant flocs, compared to the additional removal of LMW fractions by SIX. In contrast to the full clarification or clarification and SIX tests (Section 3.3.1), the addition of SIX to ILCA pretreatment yielded no appreciable fouling suppression. This was possibly due to either the change in CEB reagent (from NaOCl to NaOH), the difference in floc morphology, or, most likely, the nature of the direct filtration process where a floc cake is formed on the membrane surface. Previous research has suggested that this cake layer may reduce irreversible membrane fouling by either adsorbing some unflocculated organic compounds, and therefore preventing their adsorption to the membrane (Dong *et al.* 2007), or by rejecting fine flocs or colloids which would otherwise plug the membrane pores (Guigui *et al.* 2002).

3.3.4 SIX + ILCA pretreatment with automated coagulant and pH control

A virgin membrane and an automated pH and coagulant control system was installed prior to an extended fouling rate test (21 days) at a high flux of 185 LMH on the UPRIV source water (Figure 3.4). Low fouling rates were sustained despite rapid changes in raw water quality and DOC concentration associated with heavy rainfall events. Cessation of coagulation during this trial (Day 9) led to a rapid increase in the TMP, which was ameliorated on reinstating the coagulant dose, albeit at a slightly higher baseline TMP. Taking the SIX dosing off line on Day 13 did not lead to an increased fouling rate, a stable TMP being maintained. Overall a very low fouling rate of 0.3 kPa/day was sustained despite coagulant dose upset, regardless of the resin dose, whilst operating at high flux on variable quality raw water. The results further corroborate coagulation as being the most important pre-treatment for suppressing fouling and confirmed that very low fouling rates were possible at high fluxes when operating with automated coagulant dosing and pH control. The high permeability of the virgin membrane was sustained throughout the trial. Further tests of around 2 months' duration yielded an overall fouling rate 0.24 kPa/day, with a subsequent CIP returning the membrane permeability back to that of the virgin material.

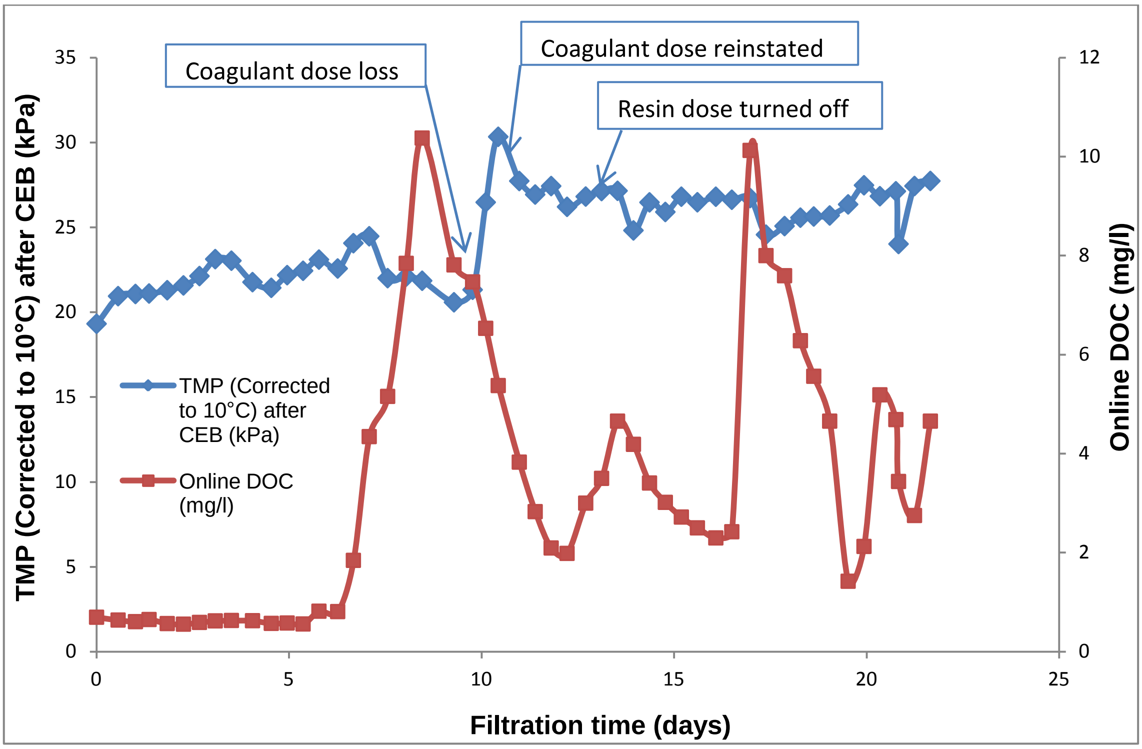

Figure 3.4 Extended operation during spate conditions (UPRIV) with automated coagulant and pH control

3.4 Conclusions

A pilot-scale study of the efficacy of pretreatment for ceramic membrane filtration of surface waters as applied to potable water supply has revealed:

- Suspended ion exchange (SIX) resin removed predominantly low molecular weight (LMW) organic matter whereas coagulation removed the high molecular weight (HMW) fractions. The combination of full clarification (coagulation with floc blanket clarification) and SIX, or SIX and in-line coagulation (ILCA) led to substantial removal of all organic fractions to leave a low residual dissolved organic carbon (DOC) concentration.
- The HMW organic compounds (present following SIX), including biopolymers, were retained by the membrane and caused rapid fouling, whereas LMW organic compounds (present following coagulation alone) were not retained when coagulation was optimised.

- Coagulation (clarification or in-line coagulation (ILCA)) largely stabilised membrane operation due to removal or enmeshment of HMW organic compounds.
- When using optimised in-line coagulation (ILCA) with direct membrane filtration, as opposed to full clarification pretreatment, additional pretreatment with SIX provided no measureable benefit with regards to membrane fouling suppression.
- Sub-optimal coagulation conditions, such as under-dosing of coagulant or inappropriate pH adjustment, resulted in rapid fouling.
- SIX ILCA pretreatment provided similar DOC removal to clarification followed by SIX pretreatment whilst providing a more compact, efficient and flexible process than clarification and SIX pretreatment.
- A fully optimised system with automated pH and coagulant control allowed operation at an elevated flux of 185 LMH on a water source of highly variable organic concentration with overall membrane fouling rates below 0.3 kPa/day over a two-month test period.

3.5 Acknowledgments

The authors would like to acknowledge:

South West Water, Exeter, U.K who funded and supported the work and South West Water Laboratories, Exeter, U.K for the provision of water analysis.

Gilbert Galjaard, Holly Shorney-Darby, Jumeng Zheng and Harry Scheerman from PWN Technologies, Netherlands for the design and build of the pilot plant and for ongoing technical support throughout the project.

RWB Water Services, Almelo, Netherlands for the design, build and ongoing assistance with maintenance of the pilot plant.

Het Water Laboratorium, Haarlem, Netherlands who provided LC-OCD analysis.

3.6 References

Bond, T., Goslan, E., H., Parsons, S., A., Jefferson, B., 2011. Treatment of disinfection by-product precursors. *Environmental Technology*, 32 (1), pp. 1-25.

Dong, B., Dong, B., Gao, N., Deng, H., Fan, J., 2005. Effect of coagulation on preventing membrane from fouling. *Huanjing Kexue/Environmental Science,* 26(1), pp. 90-93.

Fabris, R., Lee, E.K., Chow, C.W.K., Chen, V., Drikas, M., 2007. Pre-treatments to reduce fouling of low pressure micro-filtration (MF) membranes. *Journal of Membrane Science,* 289(1-2), pp. 231-240.

Fan L., Nguyen T., Roddick, F.A., Harris, J.L., 2008. Low-pressure membrane filtration of secondary effluent in water reuse: Pre-treatment for fouling reduction. *Journal of Membrane Science,* 320(1-2), pp. 135-142.

Fearing, D.A., Banks, J., Guyetand, S., Eroles, C.M., Jefferson, B., Wilson, D., Hillis, P., Campbell, A.T., Parsons, S.A., 2004. Combination of ferric and MIEX® for the treatment of a humic rich water. *Water Research*, 38 (10), pp. 2551-2558.

Freeman, S., Shorney-Darby, H., 2011. What's the buzz about ceramic membranes? *Journal of the American Water Works Association*. 103, pp. 12–13.

Galjaard, G., Martijn, B., Koreman, E., Bogosh, M., Malley, J., 2011. Performance Evaluation SIX® -CeraMac® in Comparison with Conventional Pre-treatment Techniques for Surface Water Treatment. *Water Practice and Technology*, 6 (4).

Gray, S.R., Dow, N., Orbell, J.D., Tran, T., Bolto, B.A., 2011. The significance of interactions between organic compounds on low pressure membrane fouling. *Water Science and Technology,* 64(3), pp. 632-639.

Guigui, C., Rouch, J.C., Durand-Bourlier, L., Bonnelye, V., Aptel, P., 2002. Impact of coagulation conditions on the in-line coagulation / UF process for drinking water production. *Desalination,* 147(1-3), pp. 95-100.

Hofs, B., Ogier, J., Vries, D., Beerendonk, E.F., Cornelissen, E.R., 2011. Comparison of ceramic and polymeric membrane permeability and fouling using surface water, *Separation and Purification Technology*, 79, p 365– 374

Huang, H., Schwab, K., Jacangelo, J.G., 2009. Pretreatment for low pressure membranes in water treatment: A review. *Environmental Science and Technology,* 43(9), pp. 3011-3019.

Huang, H., Cho, H., Schwab, K.J., Jacangelo, J.G., 2012. Effects of magnetic ion exchange pretreatment on low pressure membrane filtration of natural surface water. *Water Research,* 46(17), pp. 5483-5490.

Huber, S.A., Balz, A., Abert, M., Pronk, W., 2011. Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography - organic carbon detection - organic nitrogen detection (LC-OCD-OND). *Water Research*, 45 (2), pp. 879-885.

Humbert, H., Gallard, H., Jacquemet, V., Croué , J., 2007. Combination of coagulation and ion exchange for the reduction of UF fouling properties of a high DOC content surface water. *Water Research*. 41 (17), pp. 3803-3811.

Jarvis, P., Mergen, M., Banks, J., Mcintosh, B., Parsons, S.A., Jefferson, B., 2008. Pilot scale comparison of enhanced coagulation with magnetic resin plus coagulation systems. *Environmental Science and Technology*, 42 (4), pp. 1276-1282.

Kimura, K., Tanaka, K., Watanabe, Y., 2014. Microfiltration of different surface waters with/without coagulation: Clear correlations between membrane fouling and hydrophilic biopolymers. *Water Research,* 49, pp. 434-443.

Lai, C., Chou, Y., Yeh, H., 2015. Assessing the interaction effects of coagulation pretreatment and membrane material on UF fouling control using HPSEC combined with peak-fitting. *Journal of Membrane Science,* 474, pp. 207-214.

Lee, S. and Kim, J., 2014. Differential natural organic matter fouling of ceramic versus polymeric ultrafiltration membranes. *Water Research,* 48(1), pp. 43-51.

Mergen, M.R.D., Adams, B.J., Vero, G.M., Price, T.A., Parsons, S.A., Jefferson, B., Jarvis, P., 2009. Characterisation of natural organic matter (NOM) removed by magnetic ion exchange resin (MIEX® Resin) *Water Science and Technology: Water Supply*, 9 (2), pp. 199-205.

Metcalfe D., Rockey C., Jefferson B., Judd S., Jarvis P., 2015. Removal of disinfection by-product precursors by coagulation and an innovative suspended ion exchange process. *Water Research,* 87, pp. 20-28.

Meyn, T., Altmann, J., Leiknes, T., 2012. In-line coagulation prior to ceramic microfiltration for surface water treatment-minimisation of flocculation pre-treatment. *Desalination and Water Treatment*, 42 (1-3), pp. 163-176.

Myat, D.T., Mergen, M., Zhao, O., Stewart, M.B., Orbell, J.D., Gray, S., 2012. Characterisation of organic matter in IX and PACl treated wastewater in relation to the fouling of a hydrophobic polypropylene membrane. *Water Research,* 46(16), pp. 5151-5164.

Singer, P.C., Bilyk, K., 2002. Enhanced coagulation using a magnetic ion exchange resin. *Water Research*, 36 (16), pp. 4009-4022.

Subhi, N., Leslie, G., Chen, V., Le-clech, P., 2012. Organic Fouling of Ultrafiltration Membrane: Detailed Characterization by Liquid Chromatography with Organic Carbon Detector (LC-OCD). *Separation Science and Technology,* 48(2), pp. 199-207.

Shang, R., Vuong, F., Hu, J., Li, S., Kemperman, A.J.B., Nijmeijer, K., Cornelissen, E.R., Heijman, S.G.J., Rietveld, L.C., 2015. Hydraulically irreversible fouling on ceramic MF / UF membranes: Comparison of fouling indices, foulant composition and irreversible pore narrowing. *Separation and Purification Technology,* 147, pp. 303-310.

Tian, J., Ernst, M., Cui, F., Jekel, M., 2013. Correlations of relevant membrane foulants with UF membrane fouling in different waters. *Water Research,* 47(3), pp. 1218-1228.

Vreeburg J.H.G., Schippers D., Verberk J.Q.J.C., Van Dijk J.C., 2008. Impact of particles on sediment accumulation in a drinking water distribution system. *Water Research,* 42(16), pp. 4233-4242.

Wang, S., Liu, C., Li, Q., 2011. Fouling of microfiltration membranes by organic polymer coagulants and flocculants: Controlling factors and mechanisms. *Water Research,* 45(1), pp. 357-365.

Yu, W., Liu, H., Xu, L., Qu, J., Graham, N., 2013. The pre-treatment of submerged ultrafiltration membrane by coagulation - Effect of polyacrylamide as a coagulant aid. *Journal of Membrane Science,* 446, pp. 50-58.

Zheng, X., Ernst, M., Huck, P.M., Jekel, M., 2010. Biopolymer fouling in dead-end ultrafiltration of treated domestic wastewater. *Water Research,* 44(18), pp. 5212-5221.

4 Overall discussion

The aim of this discussion is to bring together the key findings from the preceding chapters and discuss whether the SIX/ILCA/CMF process may offer advantages over conventional processes for full scale water treatment of surface waters. This will focus on; the ability of the process to offer enhanced NOM removal and DBP reductions; how the residual organic compounds following pretreatments affected ceramic membrane fouling and subsequent considerations for process implementation.

4.1 Removal of DOC and organic fractions by SIX

SIX was shown to preferentially remove the lower MW organic fractions and removed slightly more overall DOC than coagulation (58-62% vs. 53-59%) for the low to moderate DOC sources. However, when DOC concentrations and specific UV absorbance (SUVA) were high during river spate conditions the removal by SIX was reduced (35%) (Figure 2.2). These data corroborate long-term DOC removal data from the study (23-63%, 51% average) and indicate good performance of the gel type resin, with DOC removal being broadly consistent with published pilot study data from resins such as MIEX (Drikas et al. 2003; Wert et al. 2005; Boyer & Singer, 2006; Shorrock & Drage, 2006; Singer *et al.* 2007; Cromphout *et al.* 2008; Mergen *et al.* 2008). Bench scale tests with MIEX typically report higher removal rates (Fearing *et al.* 2004; Boyer & Singer, 2005; Humbert *et al.* 2005) due to the higher activity of the virgin resins used (Walker & Boyer, 2011) and non standard operating conditions giving enhanced removal (Mergen *et al.* 2008). The long term SIX data from the current extensive large scale pilot plant study, including continuous ion exchange (IEX) operation and regeneration, can be considered representative of full scale operation for similar waters.

The organic fractions removed by SIX were investigated using LC-OCD analysis. SIX was shown to preferentially adsorb the lower MW humic substances (HS) and building blocks (BB) fractions, reducing their concentration by 62% on average for both fractions. The low molecular weight (LMW) neutrals

(LMW-N) fraction was reduced by 33% and the high MW (HMW) biopolymer (BP) fraction by 13%. These data (Figure 2.2 and Figure 2.3) corroborate the long term LC-OCD average removal data throughout the trial (60, 59, 34, 19% removal for HS, BB, LMW-N and BP respectively), indicating stable operation over the study's duration.

These results differ somewhat from previous studies with MIEX which typically show preferential adsorption of the humic fraction (~70-80%) and much lower removal of the BB fraction (~8-20%), BP fraction (typically <10%) and LMW-N fraction (~22%) (Shorrock & Drage, 2006; Cromphout *et al.* 2008; Grefte *et al.* 2013). This finding relates to factors such as the charge characteristics of the organic fractions, the resin type (macroporous or gel) and the regeneration regime. The findings of previous studies on the impact of regeneration regime on organic compound removal are discussed below.

Limited removal of HMW organic fractions (BPs) by IEX resins, has been widely reported and attributed to decreasing charge with increasing MW and size exclusion from the resin matrix (Croué *et al.* 1999; Humbert *et al.* 2007; Huber *et al.* 2011; Grefte *et al.* 2013). Mergen et al. (2008) showed that for a high DOC, high SUVA water (Albert WTW) the removal of HMW organic compounds rapidly diminished as the number of bed volumes (BVs) of water treated by the resin increased. This was suggested to relate to resin surface blocking preventing further adsorption of this fraction. This also led to reduced removal of other fractions, with overall DOC removal reducing from 65% for the first use (100BVs) to as low as ~4% removal after the 15th use (1500 BVs), with an overall combined DOC removal of 25% for typical MIEX regeneration conditions. Further to this, a study by Bazri *et al.* (2016) showed similar results for the BB fraction: the resin initially removed ~50% of the BB fraction for the first 100 BVs of water whilst following 300 or 600 BVs removal was reduced to 20-33%. A key novelty of the SIX process is that single pass regeneration is used: all of the resin is regenerated prior to reuse. This may explain the relatively high average removal of the biopolymer fraction (19%), since organic compounds which have adsorbed at the surface are removed after a low number of BVs thereby limiting resin blinding. The high removal of BB noted in this study may relate to frequent regeneration reducing the effects of competitive adsorption of high-affinity humic substances displacing BBs when the resin is used to treat many BVs.

Typically SIX treatment led to moderate reductions in SUVA (~15%), suggesting preferential adsorption of aromatic compounds. However this removal was variable and at times non UV absorbing organic compounds were preferentially removed leading to increased SUVA (discussed in Section 2.3.1). These variable removals are in keeping with previously reported results (Allpike *et al.* 2005; Boyer & Singer, 2005 & 2006, Shorrock & Drage, 2006) and can be related to differences in the UV absorbance of the most highly charged NOM fractions, with other factors such as size exclusion of large organic compounds (which may be UV absorbing) playing a part. The latter point is particularly pertinent in this study since the highest MW fraction (BP), which was not removed effectively by IEX, significantly absorbed UV. This finding is contrary to other work which suggests that this fraction does not typically absorb UV (Huber *et al.* 2011). A review of other LC-OCD and HPSEC data from previous studies (Appendix A) concluded that strong UV absorbance in this fraction may be more commonly associated with waters from peat soil catchments. This may relate to the presence of colloids of either protein or humin / humic-metal complex nature which cause Rayleigh-Tyndall scattering and apparent UV absorption. Further analysis of this fraction using EEM (fluorescence excitation emission matrix spectroscopy) may allow this fraction to be further characterised, since this analysis can differentiate between the presence of protein-like and humic-like organic compounds (Bridgeman *et al.* 2011).

The reduced removal noted when SIX alone was used on high DOC, high SUVA waters (typically associated with heavy rainfall events), led to insufficient removal of organic compounds for minimising negative downstream effects when resin was applied at the typical dose (18ml/l). This could be related to the surface/pore blocking effect noted by Mergen *et al.* (2008), greater proportions of organic fractions not amenable to ion exchange (IEX) in the raw water (e.g.

HMW organic compounds) and to competition from other anions, such as sulphate, which have a strong affinity for IEX resins. These effects could be minimised by increasing the resin dose, to provide a greater surface area available for adsorption in the case of HMW organic compounds. However, a more robust and sustainable method for treating waters that typically contain a lot of HMW material is to use IEX in combination with a process that would easily remove HMW compounds e.g. coagulation.

4.2 Removal of DOC and organic fractions by SIX/ILCA/CMF

Results from the study in Chapter 2 show the different preferences of SIX and coagulation for LMW and HMW organic fractions respectively (Figure 2.2 & Figure 2.3). The processes were therefore complementary and when combined gave an additional 50% DOC removal relative to the existing conventional process (Figure 2.2). The majority of the reduction in DOC (vs. coagulation alone) was attributed to increased removal of the building blocks and LMW humic substances fractions, which were recalcitrant to the coagulation process. However, the combined process was also shown to enhance the removal of the other fractions (BP and low MW neutral compounds (LMW-N)). The average removals of each organic fraction were 86, 95, 63 and 51% for the BP, humic substances (HS), building blocks (BB) and LMW-N fractions respectively (Figure 2.2). These results agreed well with the long term results of the pilot work (87, 95, 62, 55%), indicating that the removals were sustainable for treating the variable raw water sources. This broad removal of high and low MW organic fractions can be considered to increase the robustness of the process for the removal of a wide range of organic compounds, for example where organic characteristics change seasonally.

The enhanced removal of each organic fraction can be related to the two individual processes removing distinct organic compounds and/or the pretreatment with SIX enhancing the coagulation process. The likely explanation is that both of these factors contribute to some degree. Mergen *et al.* (2009) showed that a portion of the LMW organic compounds in IEX brine are recalcitrant to coagulation and the data from this study and other studies

(Figure 2.3; Humbert *et al.* 2007; Mergen *et al.* 2008) have shown clear differences in the organic compounds preferentially removed by each process. For example, the removal of HMW organic molecules by IEX is limited. As high NOM concentrations have been shown to have a detrimental effect on coagulation processes (Hurst *et al.* 2004), significantly reducing the DOC load with SIX prior to coagulation is likely to enhance the organic compound removal. This agrees with other work which has shown that MIEX followed by coagulation enhances the subsequent floc characteristics (Jarvis *et al.* 2008), whilst other studies have shown that staged coagulation can provide additional removal of organic compounds (Fearing *et al.* 2004b).

Many studies that have investigated the different selectivity of IEX and coagulation have used simple DOC measurement or HPSEC-UV to assess the organic fraction removal. HPSEC data often fails to detect the compounds classified as biopolymers using LC-OCD, due to this fraction typically not absorbing UV (Huber *et al.* 2011; Aslam *et al.* 2013). Even in cases where some UV absorption is present, when coagulation is employed HPSEC typically shows complete removal of this fraction whereas LC-OCD showed that residual non-UV absorbing BP compounds persisted after coagulation. The LMW-N fraction was also shown to be removed to a greater extent by the combined process (35-65%) in comparison to either individual process (~35% removal). As both the residual HMW (following coagulation) and LMW-N fractions did not significantly absorb UV, LC-OCD allowed for more sensitive detection of their removal due to being able to quantify the organic carbon response of non UV absorbing fractions. This method may therefore be particularly beneficial when assessing the treatment of low SUVA raw waters, or where performing process optimisation (e.g. reducing DBPFP or membrane fouling) as it allows for better understanding of the organic compounds present (non-UV or UV absorbing).

4.3 Removal of disinfection by product precursors by SIX/ICLA/CMF

The combined process reduced the raw water DBPFP by 83-97% resulting in THMFP and HAAFP reductions of 58-67% relative to the conventional treatment process (Figure 2.4). These results compare favourably with previous DBPFP studies with MIEX/coagulation processes (Figure 2.6) and other advanced NOM removal processes (Bond *et al.* 2011). This is a positive result given that most of the previous IEX studies have been performed at bench scale using virgin resin.

The reductions in DBPFP relative to conventional treatment were attributed to the increased DOC removal, selective removal of UV absorbing compounds (which are typically reactive with chlorine), removal of bromide by SIX and enhanced removal of LMW organic fractions. LMW organic compounds are considered to be reactive precursors for the formation of Br-DBPs (Farré *et al*. 2013) so their removal, along with the removal of bromide can lead to the much lower concentrations of Br-DBPs noted in this study (Figure 2.7 - 47% reduction relative to conventional treatment). These compounds have a higher mass than their chlorinated analogues and therefore provide a greater contribution to the total DBP concentration.

The additional removal of the LMW UV absorbing compounds (LMW HS and BB) in combination with the reduction in Br-DBPs could explain the reductions in specific reactivity (Figure 2.5), as the LMW HS and BB compounds (breakdown products of HS) are likely to be potent DBP precursors.

Whilst the number of DBPFP tests performed was limited (Figure 2.4), the long term LC-OCD and UVT pilot performance data was in good agreement with the results from the DOC/DBPFP study. This suggests that the results obtained were sustainable and that the process can provide robust enhanced removal of DBPs.

4.4 The effect of pretreatment / residual organic compounds on ceramic membrane fouling

Investigations into the effect of residual NOM on membrane fouling, following various pretreatments, indicated that the removal of HMW organic fractions was critical for suppressing membrane fouling. The scoping experiments showed that the biopolymer fraction, which was largely recalcitrant to removal by SIX, was retained by the membrane following this pretreatment leading to rapid membrane fouling. These data corroborate previous studies which have highlighted that biopolymers are retained by membranes (Kennedy *et al.* 2005) and are typically the primary fraction involved in membrane fouling (Fan *et al.* 2008; Kennedy *et al.* 2008; Kimura *et al*. 2014; Yamamura *et al.* 2014).

When these HMW compounds were effectively removed by coagulation, the membrane fouling rates were stabilised to a large degree, which was associated with negligible adsorption of DOC by the membrane. These data showed that LMW organic compounds were not retained by the membrane, irrespective of their concentration, when HMW organic fractions were removed or flocculated prior to the membrane filtration process. Therefore the application of SIX in addition to optimised ILCA yielded no obvious additional suppression of membrane fouling.

Pretreatment using an ILCA process as opposed to a conventional coagulation/clarification process was pursued in order to provide additional flexibility in terms of changes in flow rates, reducing the number of waste streams and significantly reducing the footprint of the infrastructure required for coagulation.

Optimising the coagulation conditions was found to be critical in achieving the lowest fouling rates when operating at high flux. Due to the variable nature of the raw waters and the manually controlled coagulant and pH correction dosing for many of the trials, periods of suboptimal coagulation occurred when the pilot was unmanned. This was typically associated with insufficient coagulant dose or coagulation pH outside of the typical operating range. In these situations rapid fouling occurred which could be linked to adsorption of organic compounds to the membrane detected by either LC-OCD or manual on-site UVT tests of the membrane feed and permeate water. UVT testing therefore provided a rapid method for assessing the adsorption of (UV absorbing) organic compounds to the membrane and for optimising conditions to minimise adsorption and therefore suppress membrane fouling.

Coagulation jar tests on a wide variety of raw waters from the three sources revealed a good correlation between the optimum coagulant dose for membrane fouling suppression and the feed water UVT. This was exploited to allow automation of the coagulant dose which was considered very worthwhile given the variable nature of the raw water sources and the importance of maintaining optimised coagulation conditions. The automated system used an online solids-compensated UVT monitor and a controller (using Equation 3-1) to provide feed forward control of coagulant dosing. Automated pH control and a new membrane were also installed at the same time and an extended run was performed on source waters which were extremely variable in terms of DOC concentration. This automated control system was shown to be capable of maintaining optimised coagulation conditions despite rapid variations in DOC associated with river spate conditions (1-10mg/l DOC). Application of the automated control system resulted in excellent membrane operation with a very low fouling rate of 0.24kPa/day over a 2 month trial at high flux (185lmh), despite rapid variations in raw water quality. During this test no change in fouling rate was noted with SIX use (on or off), further indicating that the removal of LMW organic fractions did not significantly affect membrane fouling when coagulation was optimised.

Meyn *et al.* (2012) investigated the optimisation of in-line coagulation conditions for ceramic membrane filtration at high flux (250 LMH), with the lowest fouling rates obtained being extremely similar to the results from this study. Whilst this performance was good at significantly higher flux, this study used a small monolith membrane (0.4m^2) and analogue raw water made using a NOM concentrate obtained from an IEX plant. The analogue water was therefore unlikely to have contained representative concentrations of biopolymers, due to the limited removal of this fraction by IEX which has been shown in this study. Due to the importance of this fraction for membrane fouling the results reported may be unrepresentative of full scale operation. Another pilot study by Lerch *et al.* (2005) was undertaken treating natural river water using a small monolith membrane (0.4m^2). Although the membrane was operated at a lower flux of 80 LMH, the study indicated that by optimising coagulation conditions, a negligible fouling rate could be attained.

The significance of this work is that changeable natural waters from three flowing sources were supplied to the pilot plant in the same way that they would be supplied to the existing full scale treatment facility. In addition, the large scale and extended continuous operation of the pilot plant is unusual. A full scale 25m^2 third generation Metawater membrane, rather than smaller monolith or bench scale membranes, was used in conjunction with 0.2m^3 ILCA and a 3.25m^3 SIX contactor treating flows in the order of 6m^3/hr. The membrane operational conditions in terms of filtration, backwash, CEB and CIP were also typical of those used for full scale operation. Therefore, the data provided from this study more accurately reflects the hydrodynamic and operational conditions of full scale ceramic membrane operation. These factors, coupled with the use of natural surface waters and testing over an extended period assist in providing representative information for full scale design.

The results gained from this study indicate that ceramic membranes can be operated at high flux on variable natural surface waters with low fouling rates, providing coagulation conditions are optimised. The ability to run at high flux reduces capital costs whilst maintaining low fouling rates reduces the operational costs associated with labour and chemical costs for CIP.

4.5 Considerations for process implementation

Benefits associated with the removal of ~50% DOC by SIX on downstream processes include; significantly reduced coagulant and alkali dosing (where coagulation is employed), reduced sludge production and enhancement of coagulation processes, due to the lower NOM concentration of the feed water. In addition to this reduction in DOC, further reductions in coagulant dose may be possible due to removing the need for formation of a settleable floc, when a membrane barrier is used with ILCA pretreatment. Whilst in the UK, water treatment sludge is typically disposed of to land or to waste water treatment works (WWTW) at relatively low cost, changes to the acceptable disposal routes or the cost of disposal to land/WWTW may increase the importance of reducing sludge volumes in future (Keeley *et al.* 2014).

The combined process provided more robust, significantly enhanced removal of DOC due to the complementary nature of the IEX and coagulation processes for the removal of a wide range of organic compounds. This provides a range of benefits for downstream processes including; reduced chlorine demand and DBPFP, improved biostability, reduced energy usage for UV or AOP processes (due to higher, more stable treated water UVT) and greater efficiency of GAC for pesticide removal (due to reduced competition and pore blocking by NOM) in addition to extending the periods between required regeneration (which comes at significant cost) (Kennedy *et al.* 2015).

The significantly enhanced removal of DBP precursors offers water utilities a means of ensuring compliance with regulatory standards and the requirement to ensure that all water supplied “does not contain any micro-organism, parasite or substance at a concentration or value which would constitute a potential danger to human health” (DWI, 2000). Whilst THM and HAA are the dominant DBPs formed during disinfection with chlorine, hundreds of other DBPs are also formed (Richardson *et al.* 2007), with little being known about the potential toxicity of many DBPs present in drinking water. The management of water supply in the UK has increasingly shifted towards a risk based approach to water safety and regulation. Emerging DBPs which are not currently subject to specific standards are now covered by the regulatory requirement to “minimise disinfection by-products” (DWI, 2000). Therefore, emerging DBPs which are found to pose a risk to health may be more strictly controlled in future, potentially leading to the requirement for advanced water treatment processes to minimize their occurrence. Due to the robust removal of a range of organic DBP precursors by SIX/ILCA/CMF, the process provides additional mitigation against risks associated with future challenges in terms of DBPs or more stringent regulation.

The SIX/ILCA/CMF or ILCA/CMF process was shown to be able to treat variable quality source waters at high flux with low membrane fouling rates, using a simple automated feed forward coagulant dosing system based on the feed water UVT. Providing automation of the coagulant process leads to a simple, automatable treatment process requiring less intervention to robustly produce stable treated water quality in comparison with conventional treatment. Whilst the automated coagulant dosing worked very well for the high SUVA sources studied, changes in the character of the organic compounds (charge density to UV absorbance ratio), may result in unoptimised dosing. This automated system can however be used in concert with other indicators of suboptimal coagulation for membrane filtration including; alarms to alert operators of increased TMP slope (indicating increased membrane fouling associated with adsorption of DOC) and manual UVT measurements of the feed and permeate water.

Due to the critical nature of optimised coagulation for suppressing membrane fouling, other techniques for optimising coagulation conditions should be investigated. Zeta potential measurement has been shown to be a useful tool for improving coagulation in conventional treatment processes (Sharp *et al.* 2006). This technique should be explored for optimising coagulation prior to ceramic membrane filtration as a limited number of studies have also shown it to be beneficial for; reducing pore plugging (due to enhanced floc formation), improving the cake layer permeability and enhancing removal of the cake layer by BW or CEB, leading to reduced membrane fouling (Weisner *et al.* 1989; Judd & Hillis, 2001).

The footprint of SIX/ILCA/CMF is approximately 50% smaller than that required for a conventional treatment process, significantly reducing land and building requirements. This is primarily due to the high rate ILCA process significantly reducing the required footprint compared to conventional clarification infrastructure. In addition, the membranes occupy a much smaller area than would be required for RGFs. This reduction is attributed to a) the ability to run at high flux and b) the CeraMac design, where multiple membranes (192) are packed within the same membrane vessel, resulting in a large membrane surface area (4800m^2) within a small footprint (12.56m^2).

SIX pretreatment was found to provide limited benefit for membrane fouling when combined with optimised ILCA, so the SIX resin dose can be adjusted in line with the raw water quality to meet the treated water goals and ensure efficient operation of downstream processes. SIX salt use and waste stream production can therefore be reduced by using lower doses of resin during periods of low raw water NOM concentration.

Whilst a cost assessment is outside of the scope of this thesis, SWW have decided to build a full scale WTW based on this technology, due to the water quality and operational benefits that the process offers, at broadly similar whole life costs (as determined by SWWs Cost Engineers). These costs are inherently site specific. However, in the case being considered here, the added operating costs for resin, regeneration and pumping through the membranes, could be offset against reduced chemical dosing (coagulant, alkali and chlorine), reduced maintenance and labour requirements and reduced costs for GAC regeneration, resulting in slightly lower projected operational expenditure (OPEX) costs.

The SIX process produces a brine solution which for the SWW project will be disposed of at low cost to a large WWTW which is already influenced by saline intrusion. However, where low cost disposal of brine to the environment or to WWTW is not feasible, additional OPEX costs may be incurred to treat or dispose of this waste stream.

5 Conclusions

A long term, large scale pilot study of the SIX/ILCA/CMF process was conducted using three UK surface waters, whilst operating the pilot processes under conditions which were suitable for full scale treatment. This assessed the removal of DOC and DBPFP in comparison to conventional treatment and the effects of residual organic fractions, following pretreatment, on ceramic membrane fouling and the subsequent sustainable flux rate. From this study the following conclusions can be drawn:

- SIX removed similar quantities of DOC to coagulation when raw water DOC was low to moderate. However, during periods of high DOC and SUVA following heavy rainfall the removal of DOC by SIX was reduced, which led to insufficient DOC removal for reducing negative effects upon downstream processes and DBPFP (when SIX was applied as the only pretreatment).
- SIX and coagulation displayed different preferences for LMW and HMW organic fractions respectively. The processes were therefore complementary and when combined, DOC removal was significantly enhanced relative to coagulation alone. The enhanced removal was primarily due to enhanced removal of LMW HS and BB fractions although additional removal of the BP and LMW-N fractions was also noted. This led to a ~50% reduction in treated water DOC relative to an existing conventional treatment process, with associated benefits for the efficacy of downstream processes and reduced DBP concentrations.
- The SIX/ILCA process significantly reduced DBPFP relative to conventional treatment (62%) due to enhanced DOC removal, the selective removal of UV absorbing organic compounds and removal of bromide, which led to reduced specific reactivity of the residual organic fractions and reduced formation of brominated DBPs (47%).

- IEX pretreatment alone could not control ceramic membrane fouling effectively, due to limited removal of HMW organic compounds (biopolymers) which were subsequently retained by the membrane, leading to membrane fouling. The removal of biopolymers by in-line coagulation pretreatment stabilised membrane operation, leading to negligible adsorption of DOC and low membrane fouling. When coagulation conditions were optimised the fouling rate was independent of whether SIX was employed to remove additional LMW organic compounds. Therefore, SIX was not essential for membrane fouling suppression, allowing the resin dose to be tailored for the raw water conditions to meet treated water goals.
- Maintaining optimal coagulation conditions was critical for optimal membrane operation. The coagulant dose was automated using simple feed forward control from online feed water UVT measurements and this was shown to be capable of maintaining optimal coagulant dosing during rapid and extreme variations in raw water quality. Very low membrane fouling rates (0.24kPa/day) were obtained using the automated system despite operating at high flux (185 LMH) on variable raw waters over an extended test.
- The SIX/ILCA/CMF process offers benefits over conventional treatment as it is a more compact, flexible and automatable water treatment process, capable of treating variable source waters whilst providing more robust and enhanced removal of DOC and DBP precursors.

6 Further work

This work has shown the different organic fraction preferences of SIX and ILCA and how the removal of organic compounds can be enhanced when the processes are combined (using LC-OCD analysis), leading to significant reductions in DBPFP. It has also shown that ceramic membranes can be operated at high flux with low fouling on variable source waters, but it highlighted the importance of maintaining optimised coagulation conditions for suppressing membrane fouling. Further work should therefore focus upon:

- Further trials of methods for robust automation of coagulant dosing for membrane fouling suppression. The simple feed forward control system (based on UVT) worked well for the high SUVA waters tested in this study, but other methods may be required for low SUVA waters or those that contain significant particulate material which exerts a high coagulant demand. Zeta potential analysis potentially offers a useful tool for optimising coagulation because being able to assess and control the charge of colloids in the membrane feed solution may provide significant benefits to further improve membrane operation.
- Further characterisation of the UV absorbing biopolymers would be beneficial for a better understanding of the variability of compounds that can contribute to this fraction. A fuller understanding of why the biopolymers from all three raw waters used in this study absorb UV (whereas in most waters they do not), may be useful for assessing any potential impacts upon water quality and water treatment processes e.g. DBPFP and membrane fouling.
- Ceramic membranes provided a robust, automatable filtration process for the raw waters tested. Further research into the use of in-line/conventional coagulation (with or without SIX) and ceramic membranes for treating different water types would be beneficial e.g. algal dominated water sources.

REFERENCES

Aslam, Z., Dixon, M., Chow, C.W.K., Morran, J., Drikas, M., van Leeuwen, J.A., 2013. Chemometric approaches to data assessment for a long-term case study of MIEX pretreatment performance. *Desalination and Water Treatment*, 51 (16-18), pp. 3639-3649.

Bazri, M.M., Martijn, B., Kroesbergen, J., Mohseni, M., 2016. Impact of anionic ion exchange resins on NOM fractions: Effect on N-DBPs and C-DBPs precursors. *Chemosphere,* 144, pp. 1988-1995.

Bond, T., Goslan, E., H., Parsons, S., A., Jefferson, B., 2011. Treatment of disinfection by-product precursors. *Environmental. Technology*. 32 (1), 1-25.

Boyer, T.H., Singer, P.C., 2005. “Bench-scale testing of a magnetic ion exchange resin for removal of disinfection by-product precursors”, *Water Research,* 39, pp 1265-1276

Boyer, T.H., Singer, P.C., 2006. A pilot-scale evaluation of magnetic ion exchange treatment for removal of natural organic material and inorganic anions*. Water Research*, 40 (15), pp. 2865-2876.

Bridgeman, J., Bieroza, M., Baker, A., 2011. The application of fluorescence spectroscopy to organic matter characterisation in drinking water treatment. *Reviews in Environmental Science and Biotechnology,* 10 (3), pp. 277-290.

Cromphout, J., Verdickt, L., Martin, E., Vanhoucke, R., Vanhullebusch, T., 2008. Comparison between magnetic ion exchange resin-ultrafiltration and enhanced coagulation-filtration for the treatment of an NOM loaded surface water. *Water Science and Technology: Water Supply*, 8 (6), pp. 643-651

Croué, J.-P., Violleau, D., Bodaire, C., Legube, B., 1999. Removal of hydrophobic and hydrophilic constituents by anion exchange resin. *Water Science and Technology*, 40 (9), pp. 207-214.

Drikas, M., Chow, C.W.K., Cook, D., 2003. The impact of recalcitrant organic character on disinfection stability, trihalomethane formation and bacterial regrowth: An evaluation of magnetic ion exchange resin (MIEX®) and alum coagulation. *Journal of Water Supply: Research and Technology - AQUA*, 52 (7), pp. 475-487.

Drinking Water Inspectorate, 2000. The water supply (water quality) regulations 2000. Statutory Instrument, (3184).

Fabris, R., Lee, E.K., Chow, C.W.K., Chen, V., Drikas, M., 2007. Pre-treatments to reduce fouling of low pressure micro-filtration (MF) membranes. *Journal of Membrane Science,* 289(1-2), pp. 231-240

Fan L., Nguyen T., Roddick, F.A., Harris, J.L., 2008. Low-pressure membrane filtration of secondary effluent in water reuse: Pre-treatment for fouling reduction. *Journal of Membrane Science,* 320(1-2), pp. 135-142.

Farré, M.J., Day, S., Neale, P.A., Stalter, D., Tang, J.Y.M., Escher, B.I., 2013. Bioanalytical and chemical assessment of the disinfection by-product formation potential: Role of organic matter. *Water Research*, 47 (14), pp. 5409-5421.

Fearing, D.A., Banks, J., Guyetand, S., Eroles, C.M., Jefferson, B., Wilson, D., Hillis, P., Campbell, A.T., Parsons, S.A., 2004. Combination of ferric and MIEX® for the treatment of a humic rich water. *Water Research*, 38 (10), pp. 2551-2558.

Fearing, D.A., Goslan, E.H., Banks, J., Wilson, D., Hillis, P., Campbell, A.T., Parsons, S.A., 2004b. Staged coagulation for treatment of refractory organics. *Journal of Environmental Engineering,* 130 (9), pp. 975-982.

Filloux, E., Gallard, H. and Croué, J.-P., 2012. Identification of effluent organic matter fractions responsible for low-pressure membrane fouling. *Water Research,* 46 (17), pp. 5531-5540.

Grefte, A., Dignum, M., Cornelissen, E.R., Rietveld, L.C. 2013. Natural organic matter removal by ion exchange at different positions in the drinking water treatment lane. *Drinking Water Engineering and Science*, 6 (1), pp. 1-10.

Her, N., Amy, G., Mcknight, D., Sohn, J., Yoon, Y., 2003. Characterization of DOM as a function of MW by fluorescence EEM and HPLC-SEC using UVA, DOC, and fluorescence detection. *Water Research,* 37(17), pp. 4295-4303.

Huber, S.A., Balz, A., Abert, M., Pronk, W., 2011. Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography - organic carbon detection - organic nitrogen detection (LC-OCD-OND). *Water Research*, 45 (2), pp. 879-885.

Humbert, H., Gallard, H., Suty, H., Croué, J.-P., 2005. Performance of selected anion exchange resins for the treatment of a high DOC content surface water. *Water Research*, 39 (9), pp. 1699-1708.

Humbert, H., Gallard, H., Jacquemet, V., Croué, J.-P., 2007. Combination of coagulation and ion exchange for the reduction of UF fouling properties of a high DOC content surface water. *Water Research*, 41 (17), pp. 3803-3811.

Hurst, A.M., Edwards, M.J., Chipps, M., Jefferson, B., Parsons, S.A., 2004. The impact of rainstorm events on coagulation and clarifier performance in potable water treatment. *Science of the Total Environment,* 321 (1-3), pp. 219-230.

Jarvis, P., Mergen, M., Banks, J., Mcintosh, B., Parsons, S.A., Jefferson, B., 2008. Pilot scale comparison of enhanced coagulation with magnetic resin plus coagulation systems. *Environmental Science and Technology*, 42 (4), pp. 1276-1282.

Jones, M.N. and Bryan, N.D., 1998. Colloidal properties of humic substances. *Advances in Colloid and Interface Science,* 78 (1), pp. 1-48.

Judd, S.J. and Hillis, P., 2001. Optimisation of combined coagulation and microfiltration for water treatment. *Water Research,* 35 (12), pp. 2895-2904.

Keeley, J., Jarvis, P. and Judd, S.J., 2014. Coagulant recovery from water treatment residuals: A review of applicable technologies. *Critical Reviews in Environmental Science and Technology,* 44 (24), pp. 2675-2719.

Kennedy, M.D., Chun, H.K., Quintanilla Yangali, V.A., Heijman, B.G.J., Schippers, J.C., 2005. Natural organic matter (NOM) fouling of ultrafiltration membranes: Fractionation of NOM in surface water and characterisation by LC-OCD. *Desalination,* 178 (1-3 SPEC. ISS.), pp. 73-83.

Kennedy, M.D., Kamanyi, J., Heijman, B.G.J. and Amy, G., 2008. Colloidal organic matter fouling of UF membranes: role of NOM composition & size. *Desalination,* 220 (1-3), pp. 200-213.

Kennedy, A.M., Reinert, A.M., Knappe, D.R.U., Ferrer, I., Summers, R., 2015. Full- and pilot-scale GAC adsorption of organic micropollutants. *Water Research,* 68, pp. 238-248.

Kimura, K., Tanaka, K., Watanabe, Y., 2014. Microfiltration of different surface waters with/without coagulation: Clear correlations between membrane fouling and hydrophilic biopolymers. *Water Research,* 49, pp. 434-443.

Lai, C., Chou, Y., Yeh, H., 2015. Assessing the interaction effects of coagulation pretreatment and membrane material on UF fouling control using HPSEC combined with peak-fitting. *Journal of Membrane Science,* 474, pp. 207-214.

Lee, N., Amy, G. and Lozier, J., 2005. Understanding natural organic matter fouling in low-pressure membrane filtration. *Desalination,* 178 (1-3 SPEC. ISS.), pp. 85-93.

Lerch, A., Panglisch, S., Buchta, P., Tomita, Y., Yonekawa, H., Hattori, K., Gimbel, R., 2005. Direct river water treatment using coagulation/ceramic membrane microfiltration. *Desalination,* 179 (1-3 SPEC. ISS.), pp. 41-50.

Mergen, M.R.D., Jefferson, B., Parsons, S.A., Jarvis, P., 2008. Magnetic ion-exchange resin treatment: impact of water type and resin use. *Water Research*, 42 (8-9), pp. 1977-1988.

Mergen, M.R.D., Adams, B.J., Vero, G.M., Price, T.A., Parsons, S.A., Jefferson, B., Jarvis, P., 2009. Characterisation of natural organic matter (NOM) removed by magnetic ion exchange resin (MIEX® Resin) *Water Science and Technology: Water Supply*, 9 (2), pp. 199-205.

Meyn, T., Altmann, J., Leiknes, T., 2012. In-line coagulation prior to ceramic microfiltration for surface water treatment-minimisation of flocculation pre-treatment. *Desalination and Water Treatment*, 42 (1-3), pp. 163-176.

Myat, D.T., Mergen, M., Zhao, O., Stewart, M.B., Orbell, J.D., Gray, S., 2012. Characterisation of organic matter in IX and PACl treated wastewater in relation to the fouling of a hydrophobic polypropylene membrane. *Water Research,* 46(16), pp. 5151-5164.

Richardson, S.D., Plewa, M.J., Wagner, E.D., Schoeny, R., Demarini, D.M., 2007. Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research. *Mutation Research - Reviews in Mutation Research,* 636 (1-3), pp. 178-242.

Sharp, E.L., Parsons, S.A. and Jefferson, B., 2006. The impact of seasonal variations in DOC arising from a moorland peat catchment on coagulation with iron and aluminium salts. *Environmental Pollution,* 140 (3), pp. 436-443.

Shorrock, K., Drage, B., 2006. A pilot plant evaluation of the Magnetic Ion EXchange® process for the removal of dissolved organic carbon at Draycote water treatment works. *Water and Environment Journal*, 20 (2), pp. 65-70.

Singer, P.C., Schneider, M., Edwards-Brandt, J., Budd, G.C., 2007. MIEX for removal of DBP precursors: Pilot-plant findings. *Journal / American Water Works Association,* 99 (4), pp. 128-139.

Tan, Y. and Kilduff, J.E., 2007. Factors affecting selectivity during dissolved organic matter removal by anion-exchange resins. *Water Research,* 41(18), pp. 4211-4221.

Tipping, E., Rey-Castro, C., Bryan, S.E., Hamilton-Taylor, J., 2002. Al(III) and Fe(III) binding by humic substances in freshwaters, and implications for trace metal speciation. *Geochimica et Cosmochimica Acta,* 66 (18), pp. 3211-3224.

Walker, K.M., Boyer, T.H., 2011. Long-term performance of bicarbonate-form anion exchange: Removal of dissolved organic matter and bromide from the St. Johns River, FL, USA. *Water Research*, 45 (9), pp. 2875-2886.

Wert, E.C., Edwards-Brandt, J.C., Singer, P.C., Budd, G.C., 2005. Evaluating magnetic ion exchange resin (MIEX)® pretreatment to increase ozone disinfection and reduce bromate formation. *Ozone: Science and Engineering,* 27 (5), pp. 371-379.

Wiesner, M.R., Clark, M.M., Maillevialle, J., 1989. Membrane filtration of coagulated suspensions. *Journal of Environmental Engineering (United States),* 115 (1), pp. 20-40.

Yamamura, H., Okimoto, K., Kimura, K., Watanabe, Y., 2014. Hydrophilic fraction of natural organic matter causing irreversible fouling of microfiltration and ultrafiltration membranes. *Water Research,* 54, pp. 123-136.

APPENDICES

Appendix A : UV absorption of biopolymers

The 3 raw waters used in this study were all of high SUVA (typically greater than 4 L/mg-m) and they all significantly absorbed UV within the biopolymer, humic, building block and LMW humic fractions (Figure A-1). This finding, in relation to the biopolymer fraction is contrary to other work which suggests that this fraction does not typically absorb UV (Huber *et al.* 2011)

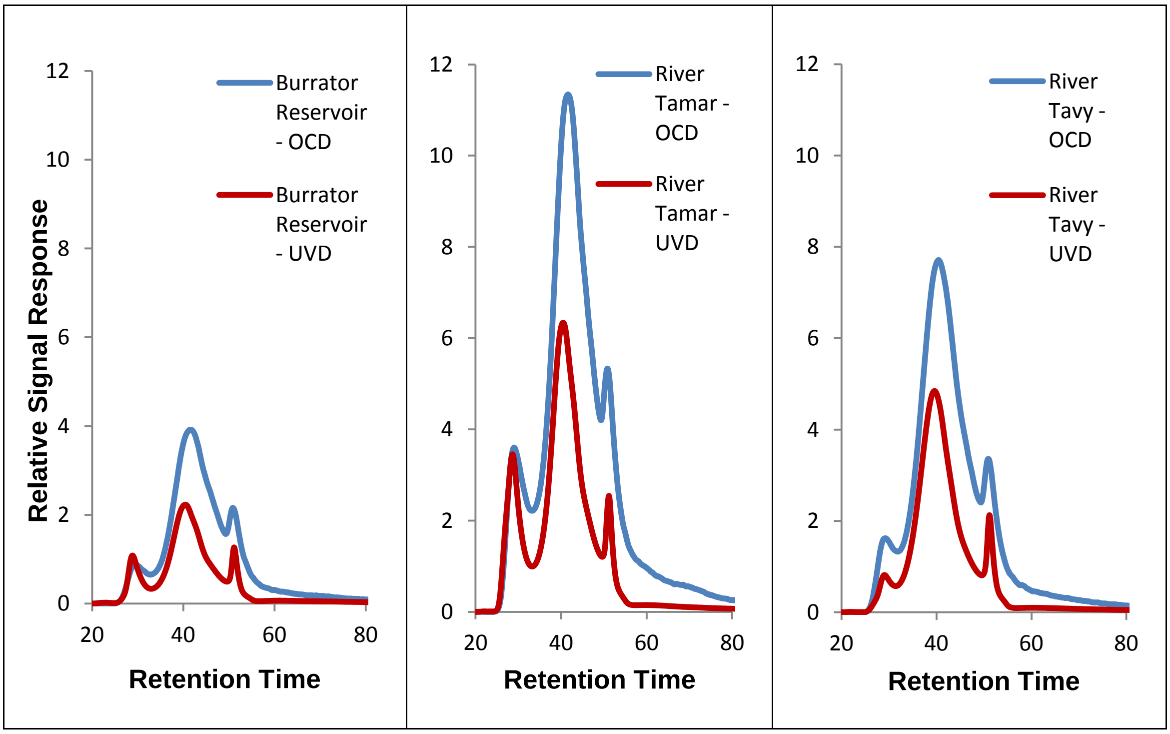

Figure A-1 LC-OCD organic carbon detection (OCD) and UV detection (UVD) for the three water sources, Burrator Reservoir (moorland reservoir within peat soil catchment), River Tamar and River Tavy (October 2013).

Only a limited number of studies conducted using LC-OCD report the UV absorbance of each fraction. Where this is reported, many studies have shown no UV absorbance (Lee *et al.* 2005; Myat *et al.* 2012; Lai *et al.* 2015) whilst others have reported slight UV absorbance within the biopolymer fraction (Humbert *et al.* 2007; Fan *et al.* 2008; Filloux *et al.* 2012; Her *et al.* 2013).

More numerous studies have been conducted with HSPEC with UV detection only; this method is therefore capable of detecting the presence UV absorbing organic compounds within a HMW peak analogous to the biopolymer peak. A number of HPSEC studies do not show the presence of a peak in this region (Humbert *et al.* 2005; Tan & Kilduff, 2007) whilst other studies report slight UV absorbance in the HMW fraction (Fabris *et al.* 2007).

Studies of four UK water sources (Fearing *et al.* 2004; Mergen *et al.* 2008 & 2009) detected UV absorbing peaks relating to HMW material by HPSEC. Although the magnitude of the spikes in relation to the organic carbon content cannot be assessed (due to only measuring the UV response), the results suggest strong UV absorbance of the HMW organic fraction, relative to the UV response of the mid MW humic substances in some of the waters.

The HMW peaks associated with moorland reservoir sources, which had very high SUVA and a predominance of HMW NOM, were much more pronounced relative to the other fractions than for 2 low SUVA sources including a lowland river and an algal laden reservoir. The samples from a moorland reservoir in a peat soil catchment (Albert WTW) showed a particularly pronounced HMW UV absorbing peak.

Based on this information and given that all of the raw water sources used in this pilot study are influenced by runoff from moorland catchments with peat soils (Dartmoor and Exmoor), high UV absorption within the biopolymer fraction may be more common in water sources influenced by peat soils. This may relate to the organic compounds present differing significantly from the typically expected polysaccharides and proteins.

A possible explanation for this finding is due to the presence of colloidal particles within this fraction which can lead to Rayleigh-Tyndall scattering of UV, manifesting as apparent absorption. In peat soil catchments, this is likely to relate to the presence of humin colloids or metal-organic complexes formed with humic substances (Jones & Bryan, 1998; Tipping *et al.* 2002). However, it should be noted that the OND (organic nitrogen detection) response for these fractions indicated low C:N ratios suggesting a significant contribution to this fraction from proteins. This is thought to be due to interference with the OND measurement from colloidal material, however, further characterisation of these UV absorbing biopolymers could help to confirm the nature of the compounds present.

Further characterisation of this fraction could be achieved through combining techniques such as separation of the biopolymer fraction (using size exclusion, membranes, dialysis etc.) followed by other organic characterisation techniques such as fluorescence excitation emission matrix spectroscopy (EEM) and analysis to establish the contribution of metals. EEM may allow this fraction to be further characterised, since this analysis can differentiate between the presence of protein-like and humic-like organic compounds (Bridgeman *et al.* 2011).