

CRANFIELD UNIVERSITY

JULIETTE W. HATT

Pretreatment Options for Municipal Wastewater Reuse Using  
Membrane Technology

SCHOOL OF APPLIED SCIENCES  
CRANFIELD WATER SCIENCE INSTITUTE

PhD THESIS  
Academic Year: 2009 -2012

Supervisor: Prof. Simon Judd  
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This thesis is submitted in partial fulfilment of the requirements for  
the degree of Doctor of Philosophy

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## **ABSTRACT**

Increasing freshwater scarcity across the world means that wastewater reclamation is being considered as a key method in which to meet the growing demand. Evolution of water reuse schemes where high quality product is required such as for indirect potable reuse has led to the adoption in recent years of the integrated membrane scheme using a combination of microfiltration or ultrafiltration with reverse osmosis membrane. However, despite technological advancements, these membranes are still prone to fouling resulting in increased costs through cleaning or replacement. This thesis aims to look at pretreatment to reduce the fouling propensity of the microfiltration membranes via a 600m<sup>3</sup>/d pilot plant which was commissioned to investigate indirect potable reuse.

A range of pretreatments including pre-screening, pre-coagulation, powdered activated carbon and granular activated carbon were assessed based on fouling amelioration, water quality improvement and cost analysis. Results showed that ferric sulphate dosing was the most effective in terms of reducing the reversible fouling rate especially at high turbidity loads enabling higher flux to be realised leading to a small cost benefit. Activated carbon proved the most effective pretreatment in terms of organic removal and a significant reduction in the irreversible fouling rate. However, the cost involved in using this as a pretreatment is significant compared to possible cost savings through reduced requirement for chemical cleaning. This pretreatment is only viable if it obviates the need for a separate organic removal process.

Keywords: Chloramine dosing, coagulation, ferric sulphate, fouling amelioration, granular activated carbon, GAC, NDMA formation, powdered activated carbon, PAC,



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## LIST OF ABBREVIATIONS

AC	Activated carbon
ANOVA	Analysis of variance
AOP	Advanced oxidation process
BOD	Biochemical oxygen demand
BV	Bed volumes
c	Coagulant mass per metre squared
CAPEX	Capital expenditure
C <sub>e</sub>	Liquid concentration
cf	Cross-flow
CIP	Cleaning in place
COD	Chemical oxygen demand
CUR	Carbon usage rate
DBP	Disinfection byproduct
DMA	Dimethylamine
DO	Dissolved oxygen
DOC	Dissolved organic carbon
dp	Differential pressure
EBCT	Empty bed contact time
FS	Flat sheet membrane
G	Velocity gradient (s <sup>-1</sup> )
GAC	Granular activated carbon
HAA	Haloacetic acids
HF	Hollow fibre membrane
HPA	Hydrophilic acids
HPN	Hydrophilic neutrals
i-o	Inside – out
id	Inside diameter
iMF	Immersed microfiltration
IMS	Integrated membrane system
IPR	Indirect potable reuse
IR	Infrared
K	Adsorbate capacity
L <sub>c</sub>	Projected coagulant cost per kilogram of coagulant
L <sub>m</sub>	Membrane cost per metre squared
LMH	Litre per metre squared per hour
MBR	Membrane bioreactor
MF	Microfiltration
MFI	Modified fouling index
MLD	Mega litre per day
MW	Molecular weight
MWCO	Molecular weight cut-off

NDMA	N-nitrosodimethylamine
NDMAFP	NDMA formation potential
NOM	Natural organic matter
o - i	Outside - in
OC	Organic carbon
OPEX	Operational expenditure
O&M	Operation and maintenance
PAC	Powdered activated carbon
PACl	Polyaluminium chloride
PES	Polyethersulphone
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene Difluoride
$q_e$	Equilibrium surface concentration
$R^2$	Coefficient of determination
RO	Reverse osmosis
SCADA	Supervisory control and data acquisition
SUVA	Specific ultraviolet absorbance
t	Membrane life
THM	Trihalomethane
TMP	Transmembrane pressure
TOC	Total organic carbon
TON	Total oxidised nitrogen
TSS	Total suspended solids
UF	Ultrafiltration
UV	Ultraviolet
UVT	Ultraviolet transmittance
WWTP	Wastewater treatment plant
1/n	Adsorbate strength



## **CHAPTER 1: Introduction**



## 1.1 Background

Increasing freshwater scarcity is becoming a worldwide issue with an estimated two-thirds of the world population predicted to be affected by the year 2025 (FAO, 2008). This has led to the consideration of alternative sources of water such as desalination and wastewater reclamation. Despite rapid development in desalination its operation is still considered costly due to its high energy consumption (Wade Miller, 2006, Gasson, 2008). Wastewater reclamation, on the other hand, makes use of a readily available source of water which varies little in volume throughout the year (Escobar, 2005). Through suitable advanced treatment following conventional secondary wastewater treatment it can be used for a range of applications such as irrigation of crops or municipal areas, wetland restoration (Mujeriego et al., 2008) and as boiler feed or cooling water for industrial users (Murrer, 2002), thereby preserving potable supplies. Alternatively it can be used to augment drinking water sources. This practice, in which the recovered water is injected into the catchment of a drinking water plant such as a reservoir (Shamloufard et al., 1995), river (Lazarova et al., 2001) or aquifer (Van Houtte and Verbauwhede, 2008, Daugherty et al., 2005), is referred to as planned indirect potable reuse (IPR). A planned IPR scheme usually consists of number of components or barriers to ensure integrity of supply. These are:

- Source control to ensure a consistent, good quality secondary treated effluent as feed to the advanced treatment process by minimising the contribution from industrial effluent.
- Conventional secondary wastewater treatment to minimise the presence of organic matter, nutrients and pathogens
- Advanced treatment to provide additional barriers to residual organic chemicals, pathogens, nutrients and dissolved solids

- Environmental buffer to provide an opportunity to chemically or physically cut the connection to the source as well as offering time to react to a process upset.
- Conventional drinking water treatment
- Comprehensive water quality monitoring and strict operating policy.

In the last 15 years (Edzwald, 2011), IPR schemes worldwide have evolved substantially in the type and sequence of treatment processes employed. This has led to the adoption in recent years of an integrated membrane system incorporating microfiltration (MF) or ultrafiltration (UF) membranes with reverse osmosis (RO) as the industry standard, especially in the United States (Markus, 2009), Singapore (Bartels et al., 2005) and Australia (Freeman et al., 2008), and including in some cases subsequent advanced oxidation processes (AOP). The MF/UF membranes act as a primary barrier to disease-causing bacteria and protozoan cysts as well as removing particulate matter which would otherwise clog the downstream RO membranes. RO removes most of the dissolved contaminants including organics, pesticides, silica and nutrients. It also removes pathogenic viruses and micro-organisms. Finally the AOP (when used) removes any recalcitrant organics and deactivates any remaining viruses (Durham et al., 2001, Freeman et al., 2008).

Despite a number of schemes worldwide using this process, much can be learned to ensure optimal running through pilot plant trials. For example, despite rapid improvements in membrane technology, membranes can still be prone to fouling problems which reduce the throughput of the process as well as increasing cost (Wilf and Alt, 2000, Bonn elye et al., 2008). Fouling propensity is dependent on the feed water to the membrane and therefore it is advisable to conduct pilot plant trials to assess the potential problems and evaluate solutions before building a full scale plant.

Thames Water, one of the regional water utilities in the UK, is investigating the use of IPR by implementing a 600 m<sup>3</sup>/d pilot plant in North London. Although the UK as a whole is not considered to be under water stress (Hochstrat et al.,

2008), eastern parts of the country receive less than 200 mm of effective rainfall (EA, 2008), which combined with the high population density leads to water resources in the Thames Water area being considered under stress from water abstraction. This problem is likely to be further exacerbated in the future by increasing population and economic growth.

## **1.2 Aims and objectives**

This thesis reports the results of a three-year research study which was fully funded by Thames Water. This thesis aims to optimise the pretreatment used at the IPR pilot plant (Figure 1-1) and reduce the downtime of the MF caused by fouling and periodic turbidity spikes in the secondary effluent feeding the IPR pilot plant.

The objectives are to:

- to evaluate and optimise the current pretreatment process, an automatic backwashing prefilter, in terms of reduced fouling (of both the prefilter and the MF) and backwashing.
- determine the effect of chloramine dosing on NDMA formation using full factorial analysis and confirm whether increasing the existing chloramine dose to >1 mg/L would lead to NDMA levels exceeding the UK regulatory action limit set by the DWI of 10 ng/L .
- evaluate the effect of chloramine dosing (at >1 mg/L as Cl) as a membrane pretreatment
- assess the use of precoagulation as membrane pre-treatment both with respect to membrane fouling and improving permeate water quality
- assess the use of powdered activated carbon as membrane pre-treatment both with respect to membrane fouling and improving permeate water quality

- assess the use of granular activated carbon bed upstream of the MF with respect to improved water quality
- compare the OPEX of each of the pretreatment method and the water quality improvement attained.

### **1.3 Thesis Structure**

This thesis is presented in paper format. All papers were written by the author, with Professor Simon Judd acting as corresponding author and Eve Germain as Thames Water reviewer on submitted journal papers. Apart from Chapter 3, all the experimental work was undertaken by the author. In the case of Chapter 3, the experimental work was partially undertaken by Cyril Lamy (MSc student from Cranfield University) as part of his MSc thesis and who was supervised by the author, Juliette Hatt.

Chapter 2 presents the findings into the use of a finer screen as pretreatment both in terms of fouling rate of the prefilter and the MF as well as the effect on water quality. The backwash sequence was also optimised to reduce downtime and water usage. This work was published in *Water Science and Technology* 63 (2011) p 2846-2852: Hatt, J.W., Germain, E. and Judd, S.J., Screening optimisation for indirect potable reuse.

Chapter 3 presents the results of a study into the effect of chloramine dose, temperature, pH and residence time on the formation of the disinfection byproduct Nitrosodimethylamine (NDMA) using full factorial analysis. This work is currently in press in *Chemosphere: NDMA formation in secondary wastewater effluent*, Hatt, J.W., Lamy, C., Germain, E., Tupper, M. and Judd, S.J..

Chapter 4 presents a study into membrane fouling reduction through the use of coagulant in-line to the microfiltration unit. The results include a basic cost analysis to assess the cost effectiveness of such a pretreatment. This work has been published in *Water Research* 45 (2011) p6471-6478: Hatt, J.W., Germain, E. and Judd, S.J., Precoagulation-microfiltration for wastewater reuse.

Chapter 5 presents the results of a laboratory and pilot scale trials using a range six of powdered activated carbons (PAC) to assess their effect on membrane fouling reduction and organics removal. This work is currently in press in Separation Science and Technology: Powdered activated carbon – microfiltration for wastewater reuse., Hatt, J.W., Germain, E. and Judd, S.J..

Chapter 6 presents the results of small GAC column trials using a range of GAC media to assess their ability to reduce both organics and turbidity and their potential as MF pretreatment. This work is currently in press in Water Science and Technology: Granular activated carbon as pretreatment for microfiltration., Hatt, J.W., Germain, E. and Judd, S.J..

Chapter 7 discusses the relative merits of each of the pretreatments evaluated within this thesis on the basis of membrane fouling reduction and improved water quality and the subsequent OPEX savings possible through reduced membrane cleaning in comparison to the OPEX costs associated with each pretreatment. This chapter details the main conclusions from this work and the interrelationship of the topics investigated.

Suggestions for further work are provided in Chapter 8.

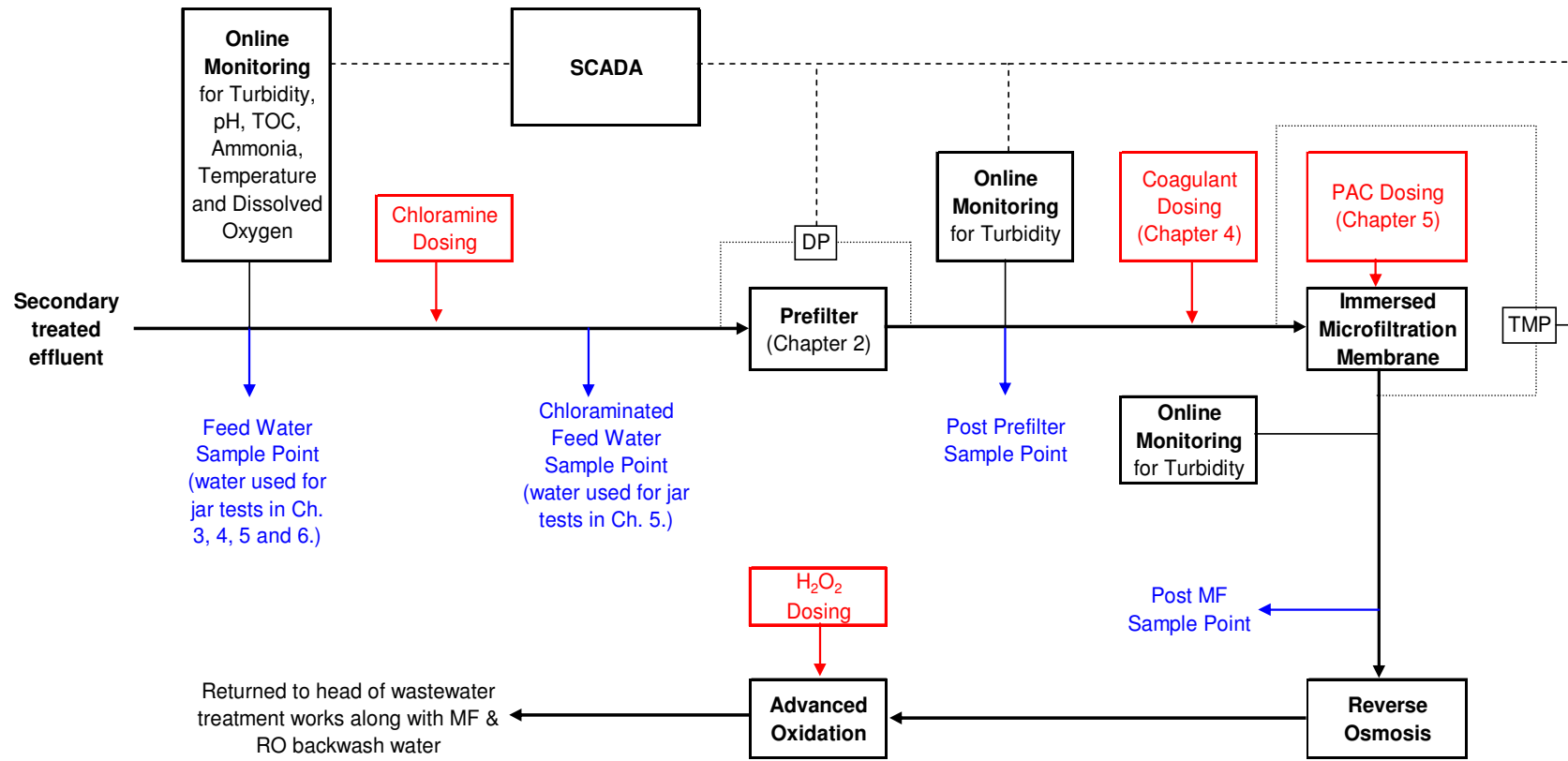


Figure 1-1 IPR Pilot Plant Process Flow Diagram



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## **CHAPTER 2: Screening optimisation for indirect potable reuse**

Hatt, J.W., Germain, E. and Judd, S.J., (2011) Screening optimization for indirect potable reuse, *Water Science and Technology*, 63, 2846-2852



## 2.1 Introduction

A combination of prolonged drought conditions in a number of countries along with a reduction in the quality of potable water supplies combined with increasing demand for potable water, has made water recycling as a supplementary water supply generally more attractive (Al-Rifai et al., 2007). Since increased demand is generally in urban areas, reuse of wastewater is made more viable by the availability of supply, matching the demand for potable water, the reduced effluent discharge to the environment, and the consistency and potentially high standard of the treated water. However, wastewater contains a high concentration of dissolved solids, pathogenic micro-organisms (Koivunen et al., 2003) and other pollutants that make it inappropriate for reuse for most non-potable duties. This has led to the development of an advanced treatment process as part of a multiple safety barrier approach to eliminate these pathogens prior to reuse of wastewater for augmenting potable water sources, known as indirect potable reuse (IPR), or as a precursor for high purity water production for industrial customers.

The multi-barrier approach includes a number of facets, the most technically germane being the use of (a) comprehensive secondary wastewater treatment, often including nutrient removal, and (b) advanced treatment process employing microfiltration/ultrafiltration (UF) membranes, reverse osmosis (RO) membranes, advanced oxidation and disinfection. The advanced treatment process itself involves multiple steps to ensure the removal of all constituents considered harmful from a public health perspective. For example, the microfiltration (MF) or UF membranes are used to remove organic and inorganic material which would otherwise cause the downstream RO membranes to rapidly foul or clog, demanding frequent chemical cleaning or membrane replacement. However, the MF/UF also acts as a primary barrier against pathogenic bacteria and protozoan cysts such as *Cryptosporidium* and *Giardia*. RO removes most dissolved contaminants including organics, pesticides, silica and single ions such as nitrate, chlorides and phosphates but also acts as a further barrier to pathogens and viruses, and to pyrogens in particular. Any

residual constituents, such as endocrine disrupting chemicals or pyrogens, may then be removed or inactivated by a downstream advanced oxidation process (AOP). Finally the water is disinfected to control biological activity in the pipework (Freeman et al., 2008, Durham et al., 2001).

Full scale plant data demonstrate that MF/UF can accommodate high feed particulates whilst still producing a filtrate of consistent quality for the RO. However, to achieve this, the frequency of backflushing and chemical cleaning needs to be adjusted to accommodate the changes in feed quality (del Pino and Durham, 1999, Durham, 1997). If the feed to the MF/UF experiences regular spikes in turbidity or is generally turbid, then the cost of frequent backflushing, in part associated with the period the membranes are offline, may be considerable. This then demands pretreatment to reduce the impact of turbidity on the MF/UF membranes.

Pre-treatment processes used at a number of reuse schemes around the world (Table 2-1) generally take the form of fine screening (or macrofiltration) using either a strainer or disk filter, usually with automatic cleaning. These screens are particularly important if there is a risk of biomass carry over from final settlement tanks of the conventional wastewater treatment process or if there is an issue with algal blooms. Consequently, the screens are generally chosen based on the MF/UF supplier recommendations to ensure the membrane warranty is not invalidated. Two major membrane suppliers recommend screen sizes of 400-500  $\mu\text{m}$  to protect the membranes from large particles, such as swarf, that may compromise membrane integrity, rather than minimise fouling. Finer screens may be recommended for protection against specific particles, such as certain types of crustacean in seawater where a screen rating of 80-100  $\mu\text{m}$  is more appropriate.

Whilst the efficacy of screening for raw sewage applications has been tested (Thompson and Marlow, 2003) and screens for MBR duties reviewed (Frechen et al., 2008), there has been no review or practical investigation of microscreening upstream of UF/MF for the recycling of treated (“secondary”)

municipal wastewater. In such instances, it is generally the case that screens must either (Table 2-1):

- be installed with automatic cleaning, such as a 150  $\mu\text{m}$  “self-cleaning” drum screen – which replaced a conventional basket screen at Flag Fen (Murrer and Macbeth, 2005).
- be sufficiently coarse to obviate cleaning, such as at the Torreele Water Reuse Scheme where a 1 mm screen has been installed apparently without detriment to the operation of the downstream MF plant (Van Houtte, 2010).

As previously mentioned, significant levels of algae may demand screening. However, despite the use of automatic cleaning, the screen originally installed at the Luggage Point Water Reclamation Plant (Barr and Hopkins, 2002) was found to blind with algae to the point where cleaning was so frequent that insufficient water was available to run the MF. This demanded that screens were cleaned externally on a weekly basis by soaking in acid to inactivate the algae – an extremely time consuming and ultimately unsustainable task. Inspection of the screen found that it was incorrectly rated. Installation of both correctly rated screen and effluent channel covers shield them from sunlight to constrain algal growth resolved these issues.

Tests of four commercially available screens revealed a drum filter retained more than three times the screenings compared with vibrating, rotating brush raked, and a rotary wedge wire screen of similar mesh size (500 – 750  $\mu\text{m}$ ) (Roderick et al., 2005). It was postulated that the use of intermittent rinsing resulted in the retention of a residual layer of sludge on the drum providing a precoat layer producing enhanced filtration. This further emphasises the importance of automated screen cleaning, and may also explain how some plants successfully use disk and drum filters with a mesh size of 60 or 150  $\mu\text{m}$ . However, there is very little published data on the operational performance of different screen types for IPR applications to enable any comparison to be

made. Specifically, there is no published information to help inform the selection of the appropriate screen mesh rating upstream of a membrane filtration plant.

This paper reports on the evaluation of an automatic backflush mesh filter for pre-treatment of secondary municipal wastewater upstream of MF/UF membranes in an IPR plant. The evaluation included operating the filter at two different mesh sizes – 500  $\mu\text{m}$  and 100  $\mu\text{m}$  – to assess whether the finer screen:

- could be sustainably operated for this application, with specific respect to the overall conversion of feed to product water as affected by backflush frequency and duration, and
- affords any significant protection to the downstream membrane process.

## **2.2 Materials and methods**

### **2.2.1 Pilot plant**

The pilot plant received effluent via a self priming centrifugal pump (Gorman-Rupp series 80) from the conventional activated sludge municipal wastewater treatment works in north London, UK. The plant comprised an automatically backflushed filter upstream of a immersed MF unit (Siemens Memcor CMF-S 0.04 $\mu\text{m}$ ), a RO unit (Hydranautics ESPA-2), and an AOP consisting of hydrogen peroxide dosing followed by high intensity UV treatment, with the product water then pH corrected prior to discharge. Chloramine could be dosed at a number of points in the process, including prior to the prefilter.

The IPR pilot plant was operated from April 2008 using 100 or 500  $\mu\text{m}$ -rated mesh prefilter, comprising in-to-out multi-wound wire elements, to protect the downstream membrane units. The prefilter was fitted with automated backflushing triggered either by a differential pressure (dp) increase of 0.38 bar across the screen or a timer set at intervals of 202 minutes. The pressure difference was monitored by a Fischer Differential Pressure Gauge model DE38.



**Table 2-1 - Summary of a selection of wastewater reuse schemes based on a dual membrane process**

Name of Scheme	On-line	Capa-city (MLD)	Use	Wastewater treatment process	Feed water quality	Pretreatment	Advanced treatment process
Luggage Point WRP, Australia	2000	14	Industrial	Secondary treatment incl. total nitrogen & phosphorus removal.	1.6NTU 12mg/l TOC	Amiad 300 µm screens	MF (Pall Filtration 0.1µm) RO (Dow TFC) (Don and Marshall, 2001, Barr and Hopkins, 2002)
Sulaibiya, Kuwait	375		Agriculture		12mg/l TSS 5mg/l BOD	Hydrotech disc filter 60µm	UF (Norit X Flow), RO (Toray TML20-400) (Gagne, 2004, Bartels, 2010)
Kranji, Singapore	2002	40	Industrial & approx. 1% for indirect potable reuse		29 -31C 5 - 29 NTU	500 µm Amiad ABF 1000 Brush Filter	MF (Siemens Memcor CMF-S S10T 0.2µm) RO (Hydranautics LFC-1) (Thompson and Powell, 2003, Coffey, 2006)
Bedok, Singapore	2002	32				500µm Amiad 1000 Brush Filter	UF (GE Water, Zenon Zeeweed), RO (Hydranautics LFC) (Coffey, 2006, Bartels, 2010)
Seletar, Singapore	2004	24				200µm Amiad 1000 Brush Filter	UF (Hyflux Kristal 300), RO (Toray ROMEMBRA) (Bartels, 2010, Coffey, 2006)
Ulu Pandan, Singapore	2006	150	Industrial			500 µm Amiad ABF 1000 Brush Filter	MF (Asahi Kasei Corp. Microza 0.1µm) RO (Hydranautics ESPA2+) (Bartels, 2010, Coffey, 2006)
Torrelee WRP, Belgium	2002	9.5	Indirect Potable Reuse	Secondary treatment - total nitrogen removal	10-22C, <15mg/l SS, 5 - 14mg/l TOC, 1mm slots <49mg/l COD	Pre-screen with 803 drum screen 150 µm	MF (Zenon (ZWC500C)), RO (Dow (BW 3LE-440)) (Van Houtte and Verbauwhe, 2008)
Flag Fen, UK	2002	1.6	Industrial		2.5 - 63mg/l TSS 2.5 - 33mg/l BOD 24 - 111mg/l COD	Hydrotech HDF 803 drum screen 150 µm	MF (Pall Filtration Microza USV6203 0.1µm) RO (Koch Membrane Systems TFC ULP) (Murrer and Macbeth, 2005)
Alamitos WRP, USA	2002	11.4	Indirect Potable Reuse	Secondary treatment	26C, 0.5NTU 1.3mg/l TSS	SP Kinney AFW-1	MF (Pall Filtration 'Microza' USV6203 0.1µm) RO (Hydranautics ESPA-2) (Fu, 2010)
Scottsdale Water Campus, USA	1999	70	Aquifer Recharge		20-32C 0.5-1.5NTU	400 µm screen	MF (Siemens Memcor CMF M10C 0.2µm) RO (Koch Fluid Systems 8832-HR TFC Magnum) (Durham et al., 2001, Vernon, 2005)
Groundwater Replenishment System, USA	2004	329	Aquifer recharge & sea water barrier			2mm rotating gravity screens	MF (Siemens Memcor CMF-S 0.2µm) RO (Hydranautics ESPA-2); UV/H <sub>2</sub> O <sub>2</sub> Trojan Tech. UV/Phox (Daugherty et al., 2005)

## **2.2.2 Analyses**

The plant was fully automated and data recorded on a supervisory control and data acquisition (SCADA) system. Online instrumentation for the prefilter included Siemens *Magflow 6000* flowmeters on the feed, discharge and backflush lines, Hach Lange turbidity and ORP meters on feed and discharge, Hach Lange pH, TOC conductivity, ammonia, and DO monitoring on the feed, and a chlorine meter on the discharge. Samples taken before and after the prefilter were also periodically taken and sent to Thames Water Laboratory for COD (total and soluble), BOD (total and soluble), total suspended solids, and TOC measurement. (Analysed using the Standard Methods for the Examination of Water and Wastewater).

## **2.3 Results**

### **2.3.1 Screen fouling assessment**

#### **2.3.1.1 Differential pressure**

The screen rating had a predictable impact on the mode of backflush actuation, with backflushing of the 500  $\mu\text{m}$ -rated screen triggered mainly by the timer and of the 100  $\mu\text{m}$  screen generally by dp.

The rate of change of pressure (fouling rate) across the pre-filter between backflushes against average raw water turbidity (Figure 2-1) indicates a linear relationship between the fouling rate and the feedwater turbidity, with the fouling propensity dependent on the screen mesh size. These relationships determine that the cleaning frequency is such that at a feedwater turbidity of 10 NTU the conversion (product vs. feed water) across the screen exceeds 99% for the 500  $\mu\text{m}$ -rated screen whilst it is less than 90% for the 100  $\mu\text{m}$  mesh screen (Table 2-2). The increased fouling rate with the 100  $\mu\text{m}$  screen also leads to an increase in energy usage of between 45 and 100% (Table 2-2). Moreover, counter-intuitively, the MF fouling rate actually increased 4-fold with the reduction in mesh size (Figure 2-2). For both 500 and 100  $\mu\text{m}$  screen ratings, the plant experienced periodic shutdown due to high resistance caused by intermittent turbidity spikes. For the range of temperature experienced over the

course of the trial (12.5 – 27.5°C), the relationship between fouling rate and turbidity was found to be independent of temperature.

### 2.3.1.2 Water quality

Spot samples taken of the raw water before and after the prefilter revealed a noticeable but none-the-less inconsistent decrease in suspended solids, BOD and COD across the prefilter with respect to the two screen sizes. On-line monitoring showed little or no reduction of turbidity at either of the two mesh sizes. This is consistent with particulate matter being present as fine solids or colloidal matter, corroborated by the observed fouling of the downstream MF membranes during turbidity spikes. On the other hand, colloidal matter cannot account for fouling of the screens.

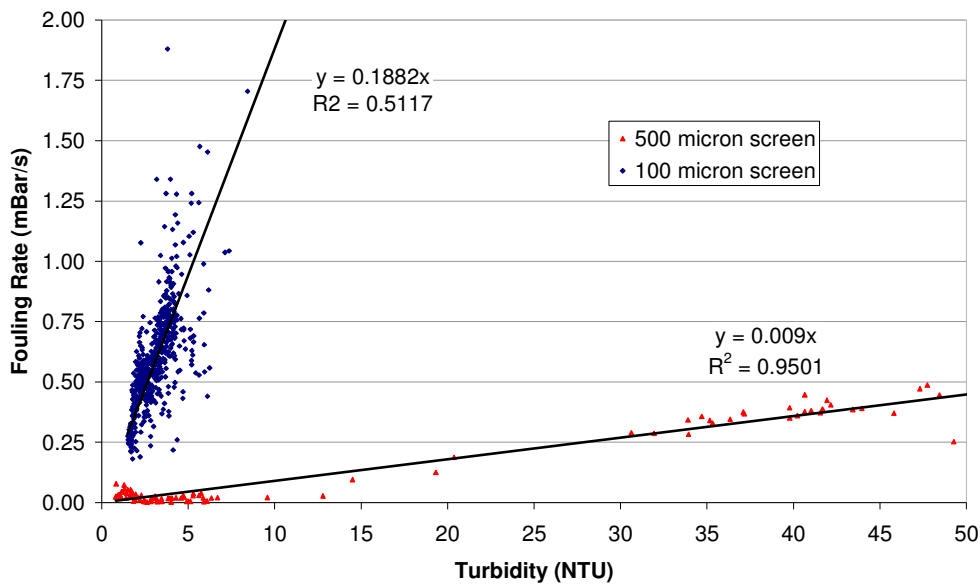
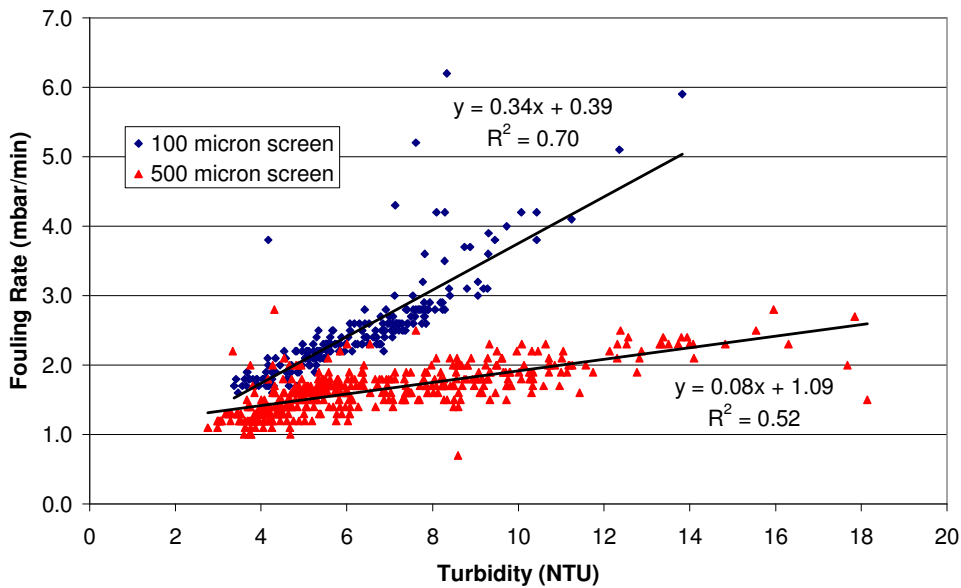


Figure 2-1 Effect of turbidity and mesh size on fouling rate of the prefilter



**Figure 2-2 Effect of turbidity and mesh size on fouling rate of the MF membranes (37 LMH, backwash every 30 minutes for 5 minutes)**

**Table 2-2 Effect of turbidity and mesh size on backflushing frequency, water usage and energy consumption**

Mesh Size ( $\mu\text{m}$ )	Turbidity (NTU)	No. of cleans per day	Daily Water Usage ( $\text{m}^3$ )	Backflush Vol./Total Produced Vol. (%)	Hydraulic Energy Consumption (kWh)
500	2	4.4	0.9	0.15	7.2
	5	11	2.3	0.36	10.2
	10	21.7	4.6	0.71	11.9
100	2	87.3	18.5	2.9	15.5
	5	192	40.8	6.3	15.9
	10	320	68.0	10.5	17.0

The root cause of the rapid fouling of the screen was investigated by dismantling the prefilter following a period of rapid fouling, which revealed a thick biofilm deposited on the permeate side of the mesh which was readily dislodged by low-pressure washing. In the normal backflush sequence this layer is not removed, since backflushing is through a reversal of the flow back through the screen rather than flowing water across it (i.e. in crossflow mode). The increased screen fouling at lower mesh sizes is thus indicative of a greater

biofilm formation propensity caused by the smaller apertures being more readily bridged by particulate matter. Increased washing is said to exacerbate this (Ingleson, 1994), and biofilm growth on the permeate side of the screen will naturally increase the likelihood of organic fouling of the membrane both due to sloughing of the film and secretion of dissolved and colloidal extracellular polymeric materials from it. This would seem to emphasise the importance of combining backflushing with permeate-side crossflow washing during the physical cleaning cycle of the finer-rated screens. While it is possible that increased selectivity of the biofouled screen removes those that particulates affording some protection of the membrane from the colloidal matter, there was no evidence of any significant and consistent difference in particle removal between the two screens.

### **2.3.2 Optimisation**

Optimisation trials conducted on the 500  $\mu\text{m}$  mesh screen aimed to minimise the backflush water volume, where backflush efficacy was assessed through monitoring of the residual dp following the backflush, which would be expected to return to a baseline level of 0.07 bar immediately after cleaning. For a turbidity below 10 NTU, the filter backflushed every 202 minutes triggered by the timer, whereas at higher turbidity levels (generally between 30 and 50 NTU) the backflush frequency increased to every 13-20 minutes in accordance with the threshold dp of 0.45 bar. However, fouling was evidently reversible since backflushing reverted to actuation by the timer following the period of high feedwater turbidity. On the other hand, reducing the backflush period to 45s (a) caused backflushing to continue actuation by threshold pressure after a turbidity peak, and (b) marginally increased the baseline dp to above 0.1 bar during normal operation (<5 NTU) and higher still during turbidity spikes.

A reduction in backflush flowrate from 8.5  $\text{m}^3/\text{h}$  to 8  $\text{m}^3/\text{h}$  resulted in ineffective cleaning as demonstrated by an increasing trend in dp immediately after cleaning. Similarly, extending the time between backflushing from 3.5 to 4 h led to a slight increase in dp post backflushing and offered little advantage overall since the highly variable nature of the feedwater quality meant that the

backflushing was only actuated by the timer 25% of the time. According to the data, the filter backflush cycle time only exceeds 3.5 hours at turbidities below 3.1 NTU for the 500 µm screen. Table 2-3 shows the effect of optimisation on the cleaning and, in particular, on water usage. At low turbidities, <3.1 NTU, the number of cleans increase but the effect on water usage was minimal since these conditions were only met 25% of the time. However, at turbidities between 3.1 and 10 NTU, the number of cleans remained the same but the backwash volume was reduced by 30% since the backwash time has been reduced by this amount.

**Table 2-3 Effect of optimisation on water usage (values in brackets represent the values pre-optimisation), 500 µm screen**

Turbidity (NTU)	No. of cleans per day	Daily Water Usage (m <sup>3</sup> )	Backflush Vol./Total Produced Vol. (%)
2	7.1 (4.4)	1.0 (0.94)	0.16 (0.15)
5	11.1 (11)	1.6 (2.4)	0.24 (0.36)
10	21.8 (21.7)	4.6 (6.8)	0.48 (0.71)

## 2.4 Conclusions

Evaluation over a 24 month period of a prefilter to MF/UF membranes, treating secondary wastewater effluent, has revealed the following:

Solids removal was negligible, and changing of the mesh size from 500 to 100 µm resulted in no evident improvement in screened water quality.

Changing from 500 to 100 µm screen mesh size produced a rapid increase in screen fouling rate due to biofilm formation on the reverse side of the mesh bridging the apertures of the finer mesh, resulting in filter blinding. This led to an increase in backflush frequency and a corresponding increase in backflush water demand by up to 20 times.

No improvement in the fouling rate of the MF membranes was experienced when the mesh size was reduced to 100 µm due to the colloidal nature of the solids present. The fact that the screen and membrane fouling rates increased with the reduction in mesh size is considered to be caused by the increased

biological load in the system caused by the build up of the biofilm on the prefilter and the shedding of organic colloidal matter from this biofilm.

With the 500 µm screen in place, optimum settings for the pre-filter were identified which ensured that the pre-filter returned to a clean state following each backflush, whilst using the minimal amount of water. These conditions equate to a backflush water volume of <0.5% of the produced volume for feedwater turbidities below 10 NTU.

The temperature range experienced during the test period had no obvious effect on performance.

## 2.5 References

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## **CHAPTER 3: NDMA formation in secondary wastewater effluent**

Hatt, J.W., Lamy, C., Germain, E., Tupper, M. and Judd, S.J., (2012) NDMA formation in secondary wastewater effluent, in press in *Chemosphere*



### 3.1 Introduction

Nitrosamines are among the most powerful of carcinogens, having been recognised since 1960 as being present in food. However, due in part to improvements in analytical methods for their detection, it was discovered in 1999 that nitrosamines, and in particular N-nitrosodimethylamine (NDMA), could occur in chlorinated drinking water at concentrations up to 10 ng/L (Najm and Trussell, 2001, Asami et al., 2009, Van Huy et al., 2011). NDMA formation is promoted when the source water has a wastewater-derived element: secondary-treated wastewater can contain a range of NDMA precursors, such as dimethylamine (DMA) and aliphatic tertiary amines with a DMA functional group (Mitch and Sedlak, 2004). During disinfection in the presence of chloramines, these precursors can form nitrosamines such as NDMA at levels in excess of 100 ng/L (Najm and Trussell, 2001, Sedlak et al., 2005). The chloramines are either added preformed or arise from the chlorination of ammonia. Thus, whilst chloramination generally leads to lower levels of disinfection byproducts (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs), NDMA formation is apparently conversely promoted.

Unlike the THM and HAA precursors, which are typically terrestrial in origin, the amine precursors of NDMA are believed to be largely anthropogenic (Bond et al., 2011). They tend to be predominantly hydrophilic, low molecular weight (low MW) compounds less than 1 kDa in size (Chen and Valentine, 2007, Pehlivanoglu-Mantas and Sedlak, 2008, Van Huy et al., 2011, Xu et al., 2011). They are consequently less amenable to removal by adsorption onto the surfaces of activated sludge and other particles present in wastewater (Pehlivanoglu-Mantas and Sedlak, 2008, Xu et al., 2011). The exception to this are those precursors present from dimethylamine-based polyacrylamide sludge thickening polymers apparently associated with particles greater than 0.7  $\mu\text{m}$  (Mitch and Sedlak, 2004). Concerns over NDMA have resulted in the World Health Organisation (2008) setting a guideline value of 100 ng/L for NDMA with some specific countries setting tighter limits. For example the UK Drinking Water Inspectorate (2008) demands monitoring when the NDMA concentration

exceeds 1 ng/L and action to reduce the NDMA concentration if it exceeds 10 ng/L; Health Canada (2011) have set a maximum acceptable concentration of 40 ng/L and the State of California an action level of 10 ng/L (2011).

Much research has been undertaken to elucidate the formation NDMA and identify possible precursors. Initial work at laboratory scale concentrated on the use of DMA as a precursor. Optimum NDMA concentration occurs when the molar ratio of DMA to monochloramine is approximately 1:1 (Choi and Valentine, 2002) and the water is saturated with dissolved oxygen. However, the yield of NDMA from DMA is low (0.5-0.6 %) (Gerecke and Sedlak, 2003, Mitch et al., 2003), even at optimum pH (pH 7-8) and with a long contact time; the high concentrations of NDMA formed from wastewater sources are thus not accounted for by this mechanism. More recent research has focused on alternative NDMA precursors such as amino-containing pharmaceuticals. Le Roux et al (2011) found that one such compound, ranitidine, provided a molar NDMA yield of 54 % at pH 7.9 which, as with a DMA precursor, rapidly decreased with decreasing oxygen content. This high yield has been corroborated by Shen and Andrews (2011), suggesting ranitidine as being a significant NDMA precursor. Meanwhile, there are ongoing investigations into the role played by the bromide ion in the formation of NDMA via chloramination of waters containing secondary and tertiary amines. At lab scale, its presence leads to an increased molar yield per mole of amine group and could explain the high NDMA formation potentials (NDMAFPs) of natural waters or wastewaters, which invariably contain bromide, as compared to model waters containing similar amounts of DMA (Le Roux et al., 2012).

Another area of significant study has concerned the influence of the order of reagent addition on NDMAFP. Najm and Trussell (2001) found NDMAFP to increase from 97 to ~600 ng/L on the addition of ammonia followed by chlorine (at a molar ratio of 4:1 chlorine:ammonia) relating to an increasing concentration from 5 to 20 mg/L as Cl<sub>2</sub>. This was attributed to an increase of dichloramine to monochloramine due to the localised high concentration of chlorine to ammonia during initial mixing, corroborated by the studies of

Schreiber and Mitch (2005) and Mitch et al (2005) on direct comparison of NDMAFP from dichloramine vs. monochloramine. However, more recent work (Le Roux et al., 2011) has shown that influence of dichloramine on NDMA formation appears to be dependent on the precursors present. Farré et al (2011) found disinfection of secondary effluents with preformed monochloramine (molar ratio chlorine:ammonia of 0.8:1), with minimal dichloramine generation, to generate significantly less NDMA than monochloramine formed in-line by chloramination. These authors showed that a secondary treated effluent could be dosed with up to 4 mg/L as Cl<sub>2</sub> as preformed monochloramine with less than 5 ng/L NDMA generated after 24 h contact time. They also demonstrated significant kinetic effects: a dose of up to 10 mg/L as Cl<sub>2</sub> could be applied independent of the dosing strategy with no more than 5 ng/L NDMA formed after 6 h, but with increasing levels subsequently.

The current study aims to establish the impact of preformed monochloramine (at 2-5 mg/l Cl<sub>2</sub>) on NDMA formation, as applied to secondary treated wastewater. The work employed factorial experimental design based on four key variables (temperature, pH, chloramination contact time and dose) to quantify the relative influence of each parameter and identify possible synergies, thus extending previous studies of temperature impacts (Mitch et al., 2003), and reagent concentration and contact time (Farré et al., 2011).

## **3.2 Materials and methods**

### **3.2.1 Experimental method**

Experiments were conducted using secondary wastewater effluent from a conventional activated sludge municipal wastewater treatment works in north London, UK (Table 3-1), all tests being carried out on the same day as sample collection. No disinfection is currently employed at the works.

The method followed was based on Standard Method 5710B (Eaton et al., 2005). Samples were adjusted to the required pH (pH 6 or 7 ± 0.2) using sodium hydroxide and/or sulphuric acid prior to buffering with 5 mL of

phosphate buffer. The pH values chosen to reflect average pH for the water under test and to enable the effect of reducing the pH during subsequent treatment for wastewater reuse to be evaluated with regards to NDMA formation. The required concentration (0, 2, 5 mg/L) of preformed monochloramine or free chlorine (as hypochlorite) was then added to the sample and completely mixed. The solutions were reacted for 1 or 24 h in the dark at 10 or 25 °C before the chlorinating agent was quenched with 8 mM sodium sulphite. Samples were then sent to the laboratory for NDMA analysis.

**Table 3-1 Feed water quality parameters, May 2011-September 2011**

	Mean	Standard deviation
Turbidity (NTU)	5.2	3.7 (71%)
TOC (mg/L)	8.6	3.0 (35%)
pH	7.0	0.5 (7%)
Temperature (°C)	19.7	1.7 (8%)
Dissolved oxygen (mg/L)	2.8	1.9 (67%)
Ammonia (mg/L)	0.10	0.06 (66%)
Alkalinity (mg/L CaCO <sub>3</sub> ) *	304	21.6 (7%)
TSS (mg/L) *	9.64	4.74 (49%)

All from continuous online monitoring other than \*based on periodic spot sampling

Preformed monochloramine stock solution was freshly prepared prior to each experiment to limit degradation by disproportionation at higher concentrations. The stock hypochlorite solution free chlorine concentration was measured immediately prior to chloramine solution preparation, and used to determine the volume required to achieve a chlorine:ammonia molar ratio of 0.2 in the monochloramine stock solution. To minimise the potential for breakpoint chlorination from localised excess of hypochlorite from poor mixing, the hypochlorite was added dropwise into a rapidly stirred solution of ammonium sulphate solution (Mitch and Sedlak, 2002).

Samples were collected in 2.5 L glass amber bottles with PTFE-lined screw lids and stored at <5 °C for no more than four hours prior to analysis. All chemicals used were of analytical grade and obtained from VWR. These included potassium dihydrogen phosphate, sodium hydroxide, sodium sulphite, sodium hypochlorite (12%) and ammonium chloride. Stock solutions were prepared in



high quality pure deionised water (Millipore). Commercial DPD (diethyl-p-phenylenediamine) test kits (Palintest) were used for site-based analysis of free and total chlorine.

### 3.2.2 Experimental design

A full factorial design was applied to these experiments to determine the significance of each factor being tested (Table 3-2) with respect to NDMA formation and the interaction between factors, with appropriate high and low values selected based on the range of normal operating conditions encountered for this application. According to a two-level full factorial design, the low and high levels (coded “+1” and “-1” respectively to provide a common scale) of each factor were combined with the two levels of every other factor used in the study, necessitating 16 experiments in total. Each experiment was repeated using a different water sample, generating 32 sets of results. Experiments were performed in a randomised order. Comparison of the mean values at each level, referred to as the “effect”, allows the impact of each factor to be quantified; the statistical significance of each factor was then determined using the t-test and ANOVA (Montgomery, 2009) using the statistical software *Minitab*, version 15.1.30.0.

**Table 3-2 Details of the factors tested and the levels used**

Factor	Uncoded Levels		Coded Levels	
	Low Level	High Level	Low Level	High Level
Monochloramine Dose (mg/L)	2	5	-1	+1
Temperature (°C)	10	25	-1	+1
Contact Time (h)	1	24	-1	+1
pH	6	7	-1	+1

### 3.2.3 Analytical methods

All analyses were carried out on site with the exception of that of the NDMA. Samples for NDMA analysis were sent to either Severn Trent or Thames Water Laboratories where the analysis was carried out using GC-MS based on US EPA Method 521 (2004) to a minimum detection limit of 3.6 ng/L. Free and total

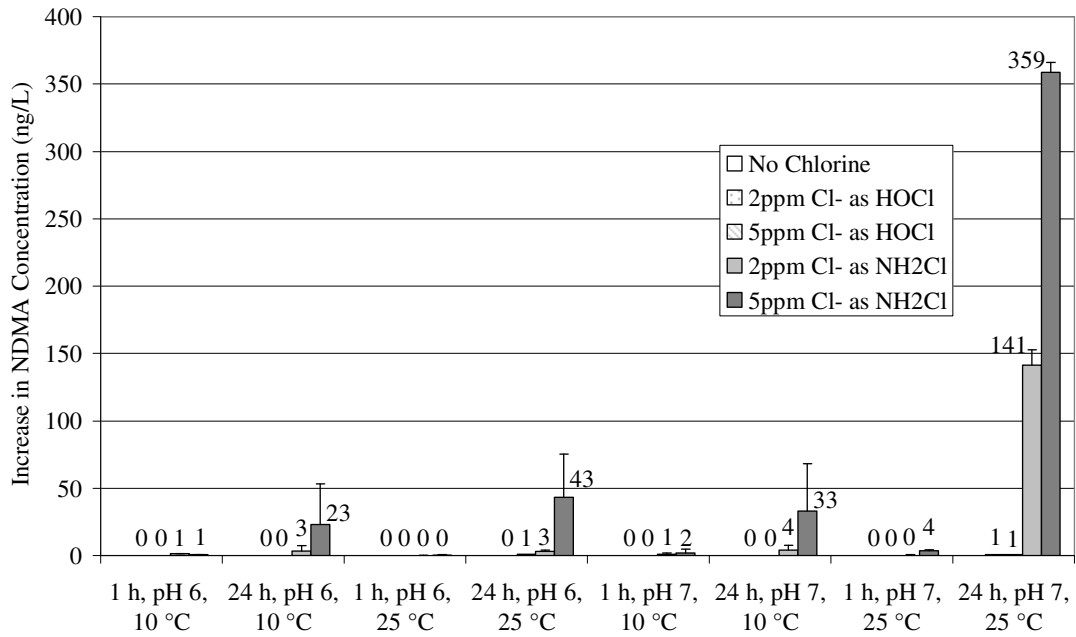
chlorine levels were measured in the final monochloramine stock solution and the hypochlorite solution using the DPD standard method developed by Palintest Ltd (UK) in conjunction with the Palintest Chlorometer. TOC and DOC were measured using a Hach Lange Astro TOC UV turbo analyser & UV<sub>254nm</sub> using a Thermo Scientific Genesys 10 Spectrophotometer.

### 3.3 Results and discussion

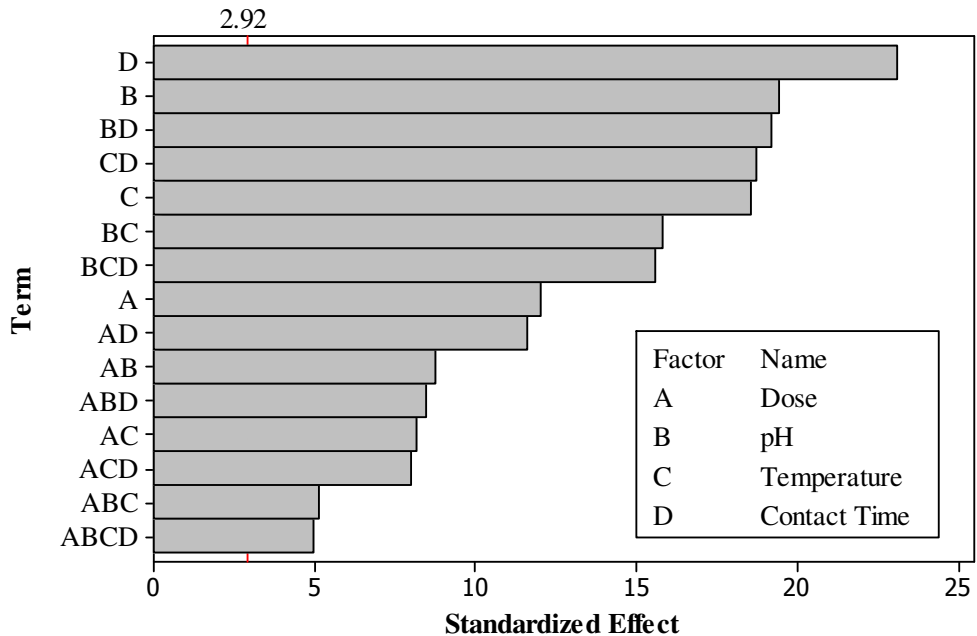
Figure 3-1 summarises the NDMA concentrations measured at the upper and lower values of chlorine form, dose, temperature, pH and contact time, and demonstrates a clear difference between dosing with chlorine and chloramines. Dosing with chlorine alone yields NDMA levels generally below the detection limit other than at long retention times and high pH and temperature, where the increase in concentration due to chlorine dosing was nonetheless  $\leq 1$  ng/L. This concurs with the findings of Choi and Valentine (2002) and Mitch and Sedlak (2004) who found a marked decrease in NDMA formation with decreasing ammonia concentration. Work by Pehlivanoglu-Mantas and Sedlak (2006) revealed NDMA precursors to form organic chloramines when chlorinated in the absence of ammonia, but not to form NDMA subsequently even when exposed to chloramines: this suggests that it is inorganic chloramines, rather than organic, that promote NDMA formation

Against this, Figure 3-1 demonstrates that dosing with chloramine generates wide-ranging NDMA levels depending on conditions employed, with an increase in contact time from 1h to 24h having the most impact and yielding NDMA concentrations exceeding the 10 ng/L action level stipulated by the UK DWI. However, applying the high levels of the other three factors (5 mg/L as Cl<sub>2</sub>, 25 °C and pH 7) also contributes to an increase in NDMA to above the 10 ng/L limit. This conflicts with the findings of Farré et al. (2011) who found that NDMA concentrations did not exceed 5 ng/L for a monochloramine dose up to 5 mg/L as Cl<sub>2</sub> with a 24 h retention time. This may well arise from the use of fully denitrified (totally oxidized nitrogen (TON)  $\leq 4$  mg/L) secondary effluent by Farré et al. (2011), such that lower levels of NDMA precursors may be expected

compared with the secondary effluent used in the current study (TON 13-28 mg/l).



**Figure 3-1 Effect of chlorine form, dose, temperature, pH and contact time on NDMA formation with error bars representing the standard deviation.**

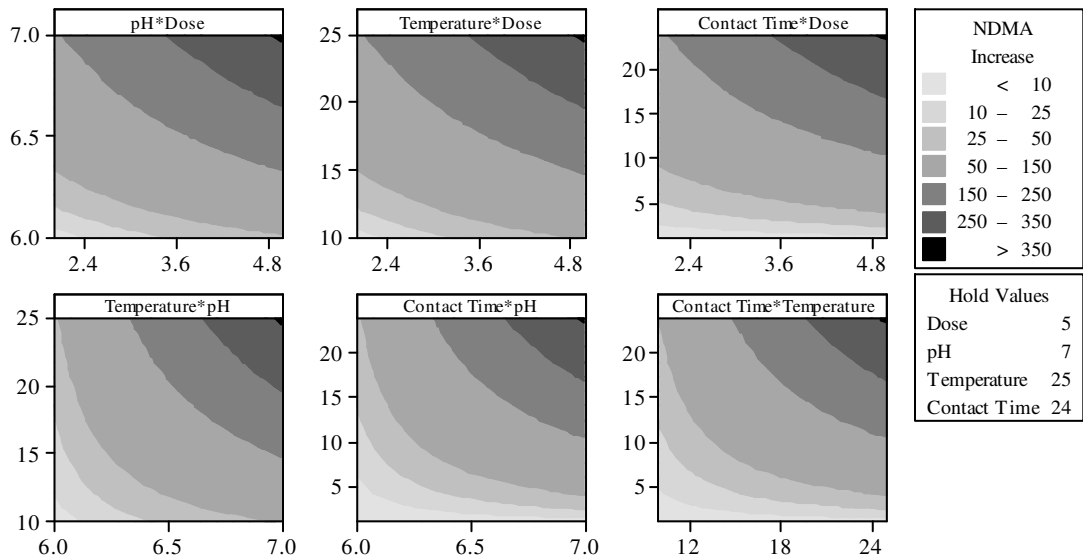


**Figure 3-2 Pareto chart showing relative magnitude and statistical significance of main and interaction effects. The reference line at 2.92 represents the 99% confidence limits.**

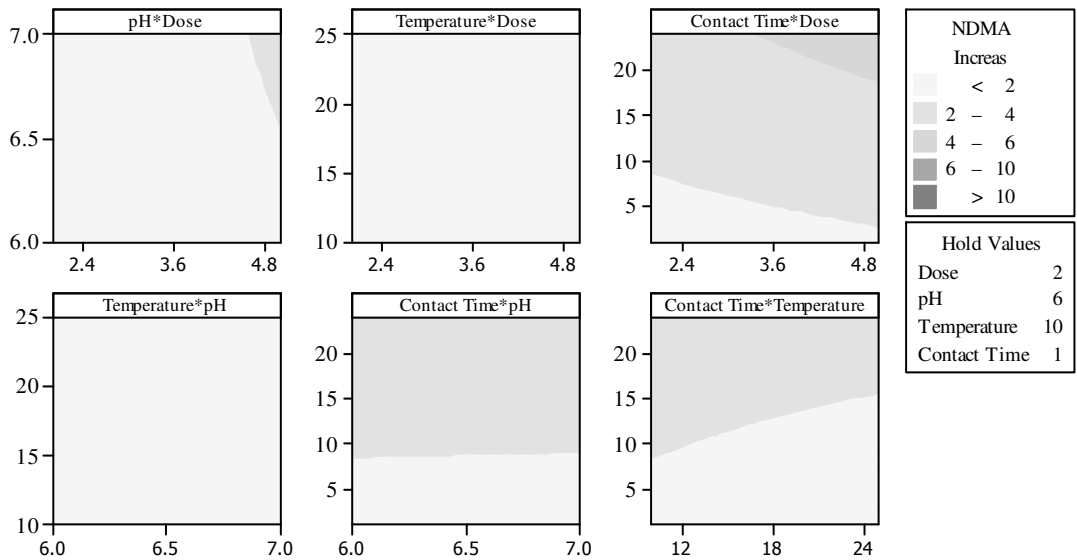
The results for the chloramine trials were analysed using the full factorial design within *Minitab* and the influence of each factor and their interactions examined using t-tests and ANOVA. The results of the analysis (Figure 3-2) indicate that all factors and their interactions can be considered statistically significant at the 99 % confidence level ( $p < 0.01$ ). Results confirm contact time as having the greatest impact on NDMAFP, approximately double the effect of dose, but shows that pH and temperature also to have a marked effect along with interactions between all three factors (Figure 3-2); further experiments are required to verify the significance of each factor and their interactions. Dose was found to have a less significant effect, suggesting that for these trials the dose used exceeded the level required to convert all of the NDMA precursors present in the final effluent. This was also reported by Choi and Valentine (2002) and Mitch et al (2003), who found NDMA levels to increase with increasing monochloramine dose until a plateau was reached due to consumption of NDMA precursors.

Whilst mean analytical data values provided a consistent trend, variation between different samples under the same test conditions was often significant (Figure 3-1). One possible explanation considered for this variation between samples was a difference in dissolved oxygen (DO) concentration, since work by Schreiber and Mitch (2006) indicated that this parameter could be significant. However, reproducing the full factor analysis including DO concentration as a covariate revealed that it was not statistically significant ( $p=0.5$ ). Another possibility is the differing levels of precursors in the secondary effluent samples as found by Pehlivanoglu-Mantas and Sedlak (2008) and Farré et al. (2011). Whilst the precursor concentrations were not measured in this work, the resulting NDMA concentrations in each test were still significantly above the 10 ng/L action level stipulated by the UK DWI.

Based on the effect calculated for each relevant factor and its interaction (Figure 3-2) a regression model can be derived, allowing the effect of factors at interim values to be predicted. Figures 3-3a and b shows the resulting contour plots created by Minitab based on this regression model. Analysis of the influence of the different factors on NDMA concentration (Figure 3-3a) reveals that if two out of the four factors are at the high level, then only a small increase in one of the other factors above the low level is likely to result in the NDMA concentration exceeding the 10 ng/L action level stipulated by the UK DWI. Against this, when two of the factors are held at their lowest values a peak concentration of 10 ng/L arises only when the contact time and dose are at their maximum value (Figure 3-3b).



a



b

**Figure 3-3** Contour plots indicating the relative influence of each pair of factors on the NDMA concentration (ng/l) when the other factors are held at a) their high values or b) their low values; dose in mg/L as Cl<sub>2</sub>, contact time in h, temperature in °C.

These figures also show the influence of temperature on NDMA concentration to be very dependent on the other conditions. According to Figure 3-3a, when

the two other factors are at high level an increase in temperature provides an increased NDMA concentration. However, Figure 3-3b shows that when two other factors are held at a low level, a temperature increase results in a slight decrease in NDMA – comparable with the results of Mitch et al (2003) who found an increase in temperature, at pH 6.5 and a contact time of 7 d, to provide a marked decrease in NDMA. This demonstrates the complexities of the NDMA formation: further testing at values between the high and low level settings is clearly required to elucidate the nature of temperature and pH impacts.

### **3.4 Conclusions**

Tests conducted on the chloramination and chlorination of a secondary wastewater which might typically considered for water reuse have confirmed that NDMA formation arises only from chloramination, with only negligible concentrations being formed from hypochlorite alone. NDMA concentrations formed varied significantly with the test conditions. A full factor analysis revealed all four factors studied (temperature, pH, monochloramine dose and contact time), both individually and synergistically, to have a statistically significant impact on NDMA formation, with contact time exerting the greatest influence.

When the raw water temperature is below 10 °C, the NDMA concentration can be minimised to below the recently promulgated 10 ng/L threshold by not exceeding a monochloramine dose of 2 mg/L as Cl<sub>2</sub>. However, at higher water temperatures other measures are required to suppress NDMA formation, such as reducing the contact time (which is likely to prove impractical in most applications) or maintaining a pH of 6 or lower. Further trials are required to fully develop the operating envelope to ensure NDMA concentrations do not exceed the suggested 10 ng/L threshold or, alternatively, effective pretreatment methods are needed to remove the NDMA precursors.

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## **CHAPTER 4: Precoagulation-microfiltration for wastewater reuse**

Hatt, J.W., Germain, E. and Judd, S.J., (2011) Precoagulation-microfiltration for wastewater reuse, *Water Research*, 45, 6471-6478



## 4.1 Introduction

A key problem encountered in the application of membrane filtration technology is fouling, which results in the loss of hydraulic performance and may reduce membrane life. Fouling can be characterised in terms of the method by which it is removed (reversible and irreversible for physical and chemical removal respectively), its chemical nature or origin (e.g. organic, inorganic, biological, etc), or its physical form (dissolved, colloidal, particulate, etc). Particulate fouling is considered to be reversible, since it is largely removed by physical cleaning. Other types of fouling may be irreversible, requiring chemical cleaning for their removal.

Much work has been aimed at elucidating fouling mechanisms to expedite its control and/or removal. Wiesner et al. (1989) concluded that particles greater than 3  $\mu\text{m}$  should not contribute significantly to membrane fouling at normal operating fluxes, but that for many membrane configurations, particles between 0.1 and 1  $\mu\text{m}$  are more likely to. The proposed use of coagulants to aggregate foulants that would otherwise plug the membrane pores dates back many years (Mietton Peuchot and Ben Aim, 1992). Studies have subsequently been undertaken to further identify the size and nature of foulants, and the coagulant types and coagulation conditions most effective in fouling amelioration (Lee et al., 2007, Howe and Clark, 2006, Howe et al., 2006). Favourable results appear to be contingent on feed water quality, membrane characteristics (such as pore size), and membrane configuration.

Jar tests have been used to determine coagulant dose and type based on organic matter removal. Work initially by Edzwald and Benshoten (1990) on surface waters revealed organic matter removal rates to be dependent on the organic matter hydrophobicity as represented by the specific ultraviolet absorbance (SUVA), the ratio of the UV light absorbance at 254 nm to the dissolved organic content. Table 4-1 demonstrates how organic matter removal rates vary with SUVA and alkalinity. Where coagulant is used on those waters with a high SUVA value and low alkalinity (<30 mg/L as  $\text{CaCO}_3$ ), high removal

rates in the range 60 – 80% can be achieved. However, those waters with high alkalinity and low SUVA, as are likely to be encountered in the trials for this paper result in particularly low removal rates of 10 – 15% despite the use of coagulant (Fan et al., 2008, Pernitsky and Edzwald, 2006).

**Table 4-1 Literature organic matter values**

Lead Author, Pub. Year	Water Source	Feedwater Quality					Coagulant	Dose (mg Me <sup>3+</sup> /L)	% TOC Removal
		TOC (mg/L)	UV (cm <sup>-1</sup> )	Alkalinity (mg CaCO <sub>3</sub> /L)	pH	SUVA L/(mg.m)			
Pernitsky (2006)	Surface	3.3	0.05	120	7.9	1.6	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> & PACI	1.5	10 - 15
Pernitsky (2006)	Surface	2.8	0.04	<30	6.7	2.2	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> & PACI	1.2	35 - 65
Fan (2008)	2ndary effluent	9.83*	0.26	190	7.1	2.6	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> , Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	2 & 5	10 - 15*
Best (2001)	Surface	2.6	0.07	11	6.8	2.8 <sup>‡</sup>	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	1	45
Pernitsky (2006)	Surface	3.1	0.09	<30	7.2	3.0	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> & PACI	1.6	60 - 80
Bagga (2008)	Surface	5.3*	0.18	57	7.5	3.4	FeCl <sub>3</sub>	15	18 - 32*
Walsh (2009)	Surface	1.72*	0.08	3.6	5.8	4.5	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.4 - 0.6	65 - 77*

\* Value is DOC not TOC. <sup>‡</sup> SUVA value is an estimate based on TOC and DOC.

Fouling suppression, however, appears not to be contingent upon organic matter removal. Work by Choi et al (2004) and Konieczny (2009) showed fouling to be suppressed at coagulant doses not significantly influencing organic matter removal. However, fouling is also affected by the plant operating and maintenance (O&M) regime, and in particular the flux or transmembrane pressure (TMP), backflush flux and frequency, and the chemical cleaning protocol. There is therefore obvious synergy between the coagulant dosing regime and the plant O&M, though few studies have focused on this synergy since many studies have been conducted on the bench scale using non-backflushable flat sheet (FS) membranes (Shon et al., 2005, Lee, 2000, Schäfer et al., 2001). Moreover, results obtained from bench-scale studies cannot be considered representative of full-scale operation due to differences in membrane module geometry and configuration, which inherently yields



differences in flux distribution and fouling rate (Yeo et al., 2006, Howe et al., 2007, Kim and DiGiano, 2006, Fane et al., 2002, Carroll and Booker, 2000).

Table 4-2 summarises studies of coagulation impacts on reversible and irreversible fouling of microfiltration/ultrafiltration (MF/UF) membranes at laboratory and pilot plant scale. Whereas reversible fouling pertains to fouling between backwashing, irreversible fouling relates to the rise in the TMP post-backwash. Results show the use of coagulant to enhance backwash efficiency, providing greater flux recovery or TMP reduction and so a reduction in irreversible fouling rate. Alum is the most widely used coagulant and can reduce the irreversible fouling rate of hollow fibre (HF) membranes by 75-100%. The dose used varies from 0.2-0.5 mg/L as Al when dosed via an aerated mixing tank to 1.3-2.5 mg/L when added inline, with no obvious correlation between dose and water quality or membrane pore size. Laboratory scale results showed much smaller reductions in the irreversible fouling rate which could be attributable to higher feedwater turbidities, differing coagulants and/or differing hydrodynamics between FS and HF membranes. Ferric chloride has given mixed results with regards to the reduction of the irreversible fouling rate. Citulski et al (2009, 2008) found that it gave rapid and irreversible fouling rate at low doses (10 – 40mg/L as Ferric Chloride), an observation corroborated by Judd and Hillis (2001) who found that at low doses the floc growth rate was insufficient to avoid pore plugging. However, at doses of 3.1 mg/L as Fe<sup>3+</sup> the same authors, (Judd and Hillis, 2001) found that the irreversible fouling rate to be reduced by 30%, corroborating previous reports elsewhere (Fan et al., 2008). Pilot scale results indicated low doses of alum ( $\leq$ 0.5 mg/L as Al) to increase reversible fouling rate, whereas doses of 1.3 – 2.5 mg/L reduce reversible fouling.

However, such papers have not considered the effect of coagulant on the relationship between turbidity and reversible fouling (Raffin et al., 2011b). Citulski et al, (2008) investigated the statistical significance of turbidity on TMP stability and, contrary to that for total suspended solids, found it to be insignificant. However, little detail was provided, other than average and

standard deviation turbidity values recorded during the trials (4.37 and 3.69 respectively). It is unclear from the report whether turbidity measurements used in the statistical analysis were daily spot samples or averages, such that the effect of turbidity spikes on fouling rates – known to be significant from operational practice - would have been overlooked.

This paper reports on the evaluation of a range of coagulants on permeability decline (manifested as the TMP increase at constant flux) on a pilot-scale MF plant treating secondary wastewater. The study concentrates on the use of coagulant at doses similar to those previously reported (Table 4-1, 0.5 – 2 mg/L) whereby coagulated organic matter removal is through charge neutralisation rather than sweep flocculation. Charge neutralisation has been shown to provide enhanced removal rates and suppressed fouling when compared with sweep flocculation (Lee et al., 2007, Lee, 2000, Pernitsky and Edzwald, 2006), notwithstanding the lower dose demanded (e.g. 0.5 – 0.7 mg/L as Al<sup>3+</sup>), and this has been attributed to the formation of a less compressible but highly porous cake under charge neutralisation conditions (Lee, 2000). The current study aims to establish the impact of fluctuations in feedwater turbidity on coagulant performance, as manifested in the reversible and irreversible fouling rates and residual dissolved organic matter concentration in the permeate product.

**Table 4-2 Summary of papers investigating the impact of coagulation on reversible and irreversible fouling of MF membranes**

Research	Raw Water	Membrane	Coagulant	Details of cleaning	Comments
Laboratory Trials					
Lahoussine-Turcaud et al (1990)	River water (2-60 NTU)	Lyonnais des Eaux PS HF (10 fibres) 1 nm pore size	Polyaluminium chloride @ $10^{-3} - 10^{-4}$ M Al	No backflush.	Initially slowed reversible fouling (first 5 h), and 10% increase in flux recovery post surface wash with demineralised water; ie reduced rate of irreversible fouling
Dong et al (2007)	River water (5-38 NTU)	Nitto Denko Corp. PVDF flat sheet 150 kDa MWCO	Alum @ 4 & 10 mg/L as Al 1min @ 100 rpm & 29 @30 rpm	Backflushed every 60mins	Coagulation reduced reversible fouling with respect to flux decline by 30% & reduced irreversible fouling by 100% ie enabled full flux recovery with backwashing
Fan et al (2008)	Secondary wastewater effluent (pH 7.1, 7.4 NTU, DOC:9.83 mg/L, CaCO <sub>3</sub> :190 mg/L)	2 different flat sheet: PVDF 0.22 µm pore size & PES 100 kDa	2 & 5 mg/L Alum as Al & Ferric Chloride as Fe	No backflush.	Coagulant reduced irreversible fouling (flux recovery increased by 30 % on MF and 13-21 % on UF
Pilot Plant Trials					
Judd and Hillis (2001)	Upland reservoir water (pH 7.44, 0.89 NTU, TOC:2.4 mg/L, CaCO <sub>3</sub> :12 mg/l)	USF Acumen Optimum PS HF (in-out) 0.1-0.2 µm pore size	Ferric chloride dosed inline, mixed using a static mixer, pH adjusted to 5.4. 0-4 mg/l as Fe	70 m <sup>3</sup> /d; const. flux (110 LMH), backflushed every 10 mins, chemically cleaned after each 24 h trial	Optimum dose of 3.1 mg/L of Fe <sup>3+</sup> reduced the irreversible fouling rate by 30%
Qin et al. (2004)	Secondary wastewater effluent (pH 7, TSS: 14.5 mg/L, COD:115 mg/L, CaCO <sub>3</sub> :100mg/L)	Norit XIGA PS HF (in-out) 0.05 µm pore size	0-4.8 mg/L Alum as Al dosed inline, using MF feed pump as mixer.	5 m <sup>2</sup> /h; const. flux. bw 2-4 times/h, Chemically enhanced backwash every 1-3 d	Min. dose 2.5 mg/L as Al <sup>3+</sup> required to stabilise the reversible fouling rate at 1.6 bar/min, full TMP recovery from backwash ie irreversible fouling rate negligible over 1 month test period
Farahbakhsh and Smith (2002)	Reservoir water (pH 6.3, 0.5 NTU, TOC 2.43 mg/l, low alkalinity)	2 different HF: Zenon Memcor 0.2 µm (both in-out);	Zenon: 4-10 mg/L Alum via aerated mixing tank. Memcor: 2-8 mg/L poly-aluminium chloride via inline static mixer	Const. flux. Zenon bw every 15-30 mins + intermittent at continuous aeration. Memcor bw every 22 mins	Coagulant increased reversible fouling rate by a factor of 2 on Zenon membrane (no info for Memcor). Backwash efficiency improved in both cases, reducing the irreversible fouling rate by approx. 75 %
Citiliski et al (2008, 2009)	Secondary wastewater effluent (pH 7.78, 4.37 NTU, COD:29 mg/l, TOC:14 mg/l)	Zenon Zeeweed 1000 (out-in). 0.02-0.1 µm pore size	Alum dosed at 10-70 mg/L and ferric chloride at 10-40 mg/L using gravity flocculation.	Const. flux, bw every 20-22 mins, 15 min soak in NaOH every 24 h and a full chemical clean when TMP = 80 kPa	Min. dose of 30 mg/L alum (1.3 mg/L as Al <sup>3+</sup> ) stabilised reversible fouling rate; negligible irreversible fouling. Ferric chloride caused rapid & irreversible fouling

## 4.2 Materials and methods

### 4.2.1 Jar Tests

Preliminary jar tests were carried out to assess the effect of the different coagulants at varying doses with reference to removal of turbidity, colour ( $UV_{400nm}$  absorption) and dissolved organic matter (DOC and  $UV_{254nm}$ ). Tests were conducted using a Phipps-Bird jar test apparatus with six flat blade paddles and two litre mixing vessels, following standard protocols (ASTM, 2003). Tests were triplicated with different water samples with no pH correction: previous reports (Table 4-1 and Table 4-2) have demonstrated measurable fouling amelioration within the pH range measured for this raw water (pH 6.7 - 7.2). The mixing conditions used were 10 s rapid mixing at  $G = 300 \text{ s}^{-1}$  followed by slow mixing for 120 s at  $G = 25 \text{ s}^{-1}$ . Samples were analysed after filtering through a  $0.45\mu\text{m}$  filter paper. These mixing conditions were chosen to replicate the hydraulic retention times and mixing regimes within the pilot plant, at the point of coagulant addition.

### 4.2.2 Pilot plant

The  $600 \text{ m}^3/\text{d}$  pilot plant has been described elsewhere (Raffin et al., 2011b), and comprised 16 immersed microfiltration (MF) membrane modules (Siemens Memcor CMF-S  $0.04 \mu\text{m}$ ). The plant received secondary effluent (see Table 4-3) from a conventional activated sludge municipal wastewater treatment works in north London, UK. The plant comprised a  $500 \mu\text{m}$ -rated automatically backflushed filter (Bollfilter model 6.18) upstream of the MF skid, the permeate then being fed to a reverse osmosis (RO) unit (Hydranautics ESPA-2) and a hydrogen peroxide-UV advanced oxidation process (AOP). Coagulants trialed were polyaluminium chloride (PACl), including a standard version (PAX-10) and a high basicity version (PAX-XL9), aluminium sulphate and ferric sulphate, all provided by Kemira Chemicals (Goole, UK). Coagulant doses refer to units of mg/L as Al or Fe. Coagulants were introduced using a peristaltic pump (Watson Marlow 520S) at a rate commensurate with their target concentration in the treated water, and dosed downstream of the MF feed pump and immediately

prior to an inline static mixer (Chemineer 2-KMS-6) and the membrane tank. The mixer and tank residence times were 10 s and 120 s respectively.

**Table 4-3 Feed water quality parameters based on continuous online monitoring**

	Average	Standard Deviation
Turbidity (NTU)	19.7	87.9
TOC (mg/L)	7.2	6.5
pH	7.0	0.2
Temperature (°C)	19.1	2.6
Alkalinity (mg/L CaCO <sub>3</sub> ) *	202.8	12.2
TSS (mg/L) *	14.4	25.8

\* Results based on periodic spot sampling

For the preliminary trials coagulant was added at doses of 0.5, 1 and 2 mg/L daily for three consecutive days for a 6-h period each day. A different coagulant was trialled each week and the MF was chemically cleaned prior to the addition of each new coagulant without pH correction. MF backflushing was every 30 minutes for 5 minutes with air and water at a flux of 45 l m<sup>-2</sup> h<sup>-1</sup> (LMH). Membrane chemical cleaning was with 540mg/L sodium hypochlorite followed by sulphuric acid at pH3, both reagents being heated to 30°C.

For the extended, week-long trials the coagulant was added at a fixed dose (0.5 mg/L) at different fluxes of 40, 45 and 50 LMH. Optimisation trials previously carried out (Raffin et al., 2011b) revealed that it was only possible to operate the MF at 50 LMH for 3-5 days between chemical cleans whereas at 40 LMH the MF could operate at a range of influent conditions with chemical cleaning at 21 day intervals. A key research objective was thus to establish whether MF operation could be sustained at 50 LMH using coagulant.

#### 4.2.3 Monitoring Analyses

Data were recorded on a supervisory control and data acquisition (SCADA) system. Online instrumentation for the MF included Siemens *Magflow 6000* flowmeters on the feed and permeate lines, Hach Lange turbidity meters on feed and permeate, and ABB pH and temperature monitoring on the discharge.

Samples taken before (pre and post coagulant addition) and after the MF were either analysed on site for TOC and  $UV_{254nm}$  or sent to the Thames Water Laboratory for total suspended solids (TSS), and residual aluminium/iron concentration measurement according to standard methods (Eaton et al., 2005). Samples were filtered using a  $0.45\mu m$  filter to provide the DOC through size exclusion comparable to that of membrane filtration. Autopsies were carried out on membrane fibre samples taken before and after each coagulant condition and treated following the method described by Porcelli and Judd (2009). The resulting eluates were also analysed by Thames Water Laboratories for a range of metals according to standard methods.

## **4.3 Results and discussion**

### **4.3.1 Jar Tests**

Results from the jar tests (Table 4-4) revealed increasing doses of coagulant to produce only a small improvement in organic matter removal rate. At the highest dose employed of 10 mg/L the measured DOC and  $UV_{254}$  removals were ~13% and ~25% respectively, the higher  $UV_{254}$  removal reflecting the preferential removal of the more hydrophobic aromatic compounds (Lahoussine-Turcaud et al., 1990, Porcelli et al., 2009, Schäfer et al., 2001, Bagga et al., 2008). These low rates of organic removal were assumed due to the low level of hydrophobicity and humic compound, as indicated by the SUVA value which ranged from 2.2 – 2.7 l/(mg.m) during the trial. Further analysis of the raw water using resin fractionation has confirmed that the hydrophobic content is in the range of 30%.

Results for organic matter removal are comparable to those previously reported (Fan et al., 2008) for waters with a similar SUVA value and high alkalinity (Table 4-1, #1 & #3 and Table 4-4). The coagulant dose applied appears to relate to the alkalinity, with the required dose increasing with alkalinity. Hence, the water in this trial required the highest dose (10 mg/L as  $Me^{3+}$ ), whereas results reported for the water having the lowest alkalinity of 120 mg/L as  $CaCO_3$  (Pernitsky and Edzwald, 2006) required the commensurately lowest dose (1.5 mg/L as Al). Thus comparison of coagulant efficacy across studies is made

challenging by the differing buffering capacities of the waters treated, given that pH adjustment to the optimum pH of ~5 is rarely carried out in wastewater coagulation.

**Table 4-4 Jar test results, showing the effect of different coagulants at varying doses on organic matter removal**

		SUVA L/(mg.m)	Quantity of coagulant added (mg Me <sup>3+</sup> /L)				
			0.5	1	2	5	10
% DOC removed	Alum	2.7	1.8	5.8	9.1	9.5	17.1
	PAX-10	2.2	0.3	3.3	5.6	9.6	15.0
	PAX-XL9	2.7	1.5	4.5	3.4	5.5	12.8
	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	2.2	3.7	4.3	5.0	6.9	9.5
% UV <sub>254nm</sub> removed	Alum	2.7	7.0	11.1	20.0	20.1	24.2
	PAX-10	2.2	5.6	8.5	13.5	14.5	29.1
	PAX-XL9	2.7	8.1	12.1	14.4	18.4	25.2
	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	2.2	6.4	7.9	8.3	9.1	10.2

### 4.3.2 Pilot Test Results

#### 4.3.2.1 Preliminary trials

Turbidity levels in the feedwater followed were found to follow a consistent diurnal cycle, such that experiments with different coagulants were carried out on consecutive days over the same time period could be assumed to be subject to a reproducible turbidity concentration transient. Statistical analysis using the student t-test on the turbidity data for each trial generally showed no significant difference between those trials with and without coagulant (  $p < 0.05$ ), the exception being the trial using 2 mg/L of PAX-XL9 where  $p = 0.10$  and somewhat lower turbidity levels were experienced.

Trials conducted at doses of 0.5-2 mg/L coagulant as Me<sup>3+</sup>, 40LMH and backflushing every 30 minutes, revealed a linear relationship between reversible fouling rate and turbidity (Figure 4-1), and irreversible fouling with time for periods of steady-state feedwater turbidity levels (Figure 4-2). However, in both cases rapid changes in feedwater turbidity produced anomalously high reversible and irreversible fouling rates. Moreover, the permeability does not

recover immediately, suggesting the single backflush sequence to be sometimes insufficient to remove high levels of contaminant loading.

**Table 4-5 Effect of coagulant at varying doses on the reversible and irreversible fouling rates**

Coagulant	Reversible fouling factor (mbar/min.NTU)				Irreversible fouling rate (mbar/d)				Turbidity load (NTU/m <sup>2</sup> ), based on a seven day period			
	Quantity of coagulant added (mg Me <sup>3+</sup> /l)											
	0	0.5	1	2	0	0.5	1	2	0	0.5	1	2
PAX-XL9		0.4	0.4	0.6		60	8	54		0.096	0.109	0.156
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.2	0.7	0.4	0.0	34	2	11	21	0.094	0.073	0.061	0.100
Alum		1.0	2.1	1.5		61	35	131		0.070	0.067	0.079

Generally the use of coagulant approximately doubled the reversible fouling factor (Table 4-5) this being the reversible fouling rate per unit turbidity (Figure 4-1). This result is comparable with that of Farahbakhsh et al (2002) who used alum doses at 4 and 10mg/L. Despite this significant increase in the reversible fouling rate, the current operational regime of backwashing at 30 minute intervals for turbidities up to 25 NTU sustained operation without exceeding the 720 mbar maximum pressure limit of the system. However, alum addition at feedwater turbidities in excess of 10 NTU resulted in a TMP rise between backwashes reaching the maximum system limit and triggering a backwash before the 30 minute interval had elapsed, increasing downtime and reducing the net flux. Ferric sulphate and PAX-XL9 had the least influence on the reversible fouling factor over the three doses applied, with ferric sulphate at 2mg/L reducing the reversible rate to a negligible level.

The irreversible fouling rate determines the time interval between chemical cleans. For zero coagulant addition the irreversible fouling rate results in a cleaning interval of approximately 3 weeks. Ferric sulphate addition resulted in the largest decrease in irreversible fouling rate, with the smallest dose resulting in the lowest recorded irreversible fouling rate of 2 mbar/d. Under these conditions, the time between chemical cleans increases from 21 days to approximately 10 months. PAX-XL9 at 1.0 mg/L also yielded a low irreversible fouling rate of 8 mbar/d, extending the time between chemical cleans to over 2



months. Conversely, alum dosing provided high levels of irreversible fouling, reducing the time between chemical cleans, despite the low and relatively stable feedwater turbidity (<5 NTU) recorded during this trial.

**Table 4-6 % Dissolved organic carbon removal during the preliminary trials**

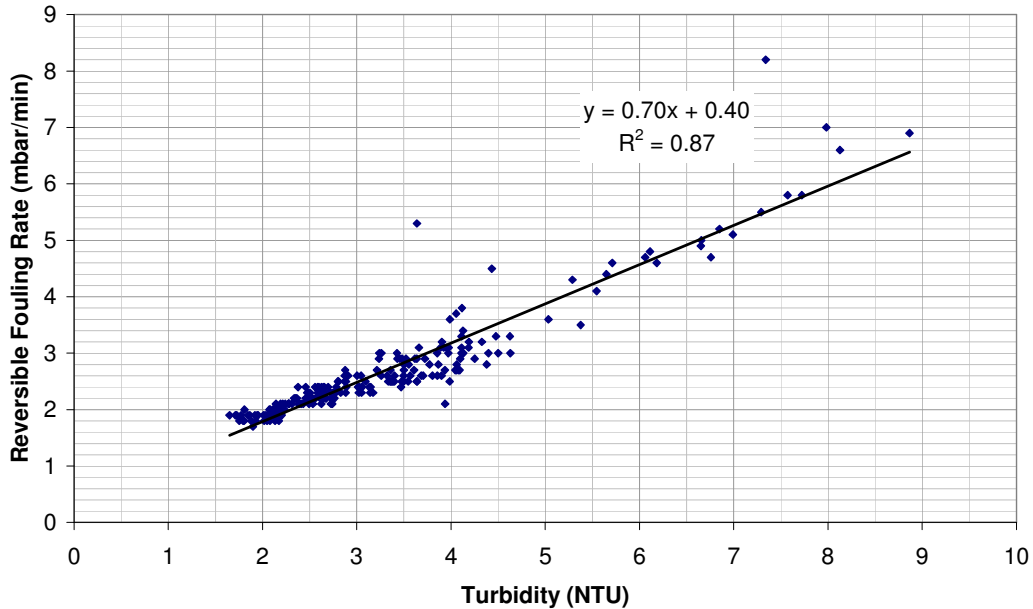
Coagulant	Quantity of coagulant added (mg Me <sup>3+</sup> /l)			
	0	0.5	1	2
PAX-10	16.4	16.5	12.8	15.5
PAX-XL9	14.2	15.6	15.4	15.1
Ferric Sulphate	13.1	10.5	12.7	12.7
Aluminium Sulphate	11.3	10.4	7.5	11.7

As expected from the jar test data, the water quality measurements revealed a negligible increase in the removal of organic matter, as DOC, with coagulant addition at low doses. (Table 4-6). No enhanced turbidity removal from coagulation arose, since the MF membranes provide excellent turbidity removal, with the MF permeate turbidity below 0.02 NTU without pre-coagulation.

Sampling of the MF permeate performed during the coagulant trials revealed the aluminium residuals to vary from 16 to 22 µg/l and the iron levels from 35 to 50 µg/l. These levels are within the normal range of permeate concentration in the absence of pre-coagulation (7-42 and 23-85 µg/L for Al and Fe respectively), indicating that coagulant dosing has no impact on the coagulant residual. This is significant, since levels above ~50 µg/l as Al would be expected to cause fouling of the downstream RO membranes through the formation of aluminium silicate; the impact of residual levels of coagulant have been found to be exacerbated at pH levels of 7.5-8.5 when alum is used as the coagulant, but not PACl, with lower pH levels of 6.7 found to reduce residual Al concentrations (Gabelich et al., 2006, Moon et al., 2009). The pH of the feed water for the current trials was in the range 6.2-7.2.

During each three-day trial, a total coagulant load of 365 g as Me<sup>3+</sup> was applied to the MF membrane modules, equating to 38 mg per metre length of membrane fibre. Autopsies performed on the membrane fibre samples taken before and after each three-day trial showed a negligible increase in metal residual post coagulant dosing (<0.01 mg per m of fibre). Autopsies performed

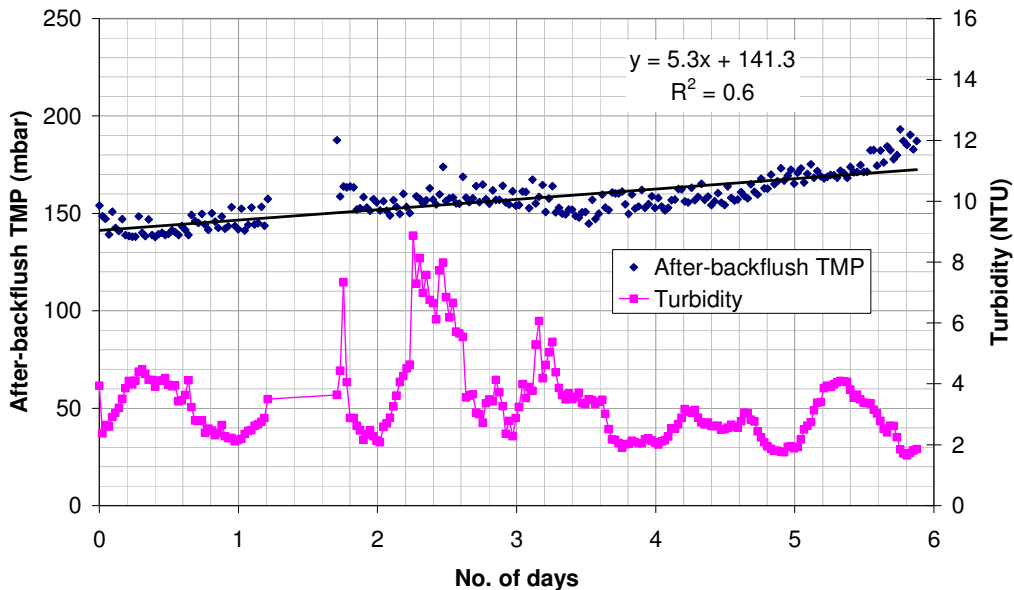
on membrane fibre samples taken after the chemical clean, (performed after each three day trial) showed that any increase in metal residual post coagulant dosing was fully removed by the chemical clean.



**Figure 4-1** The relationship between turbidity and the reversible fouling rate of the MF membrane (40 LMH, ferric sulphate dosed @ 0.5 mg/L, backwash every 30 minutes for 5 minutes, TMP corrected to 20°C)

#### 4.3.2.2 Extended trials

Further trials were performed, each over a one-week period, to assess fouling amelioration by pre-coagulation under naturally dynamic conditions of feedwater turbidity. Ferric sulphate was selected, being the coagulant displaying the most consistent suppression of reversible and irreversible fouling, according to the scoping trials, as well as being 45% lower in cost than the next best performing reagent (PAX-XL9). Each trial included the same number of diurnal cycles, and statistical analysis of turbidity data using the student t-test for each trial showed no significant difference between those trials with and without coagulant ( $p < 0.05$ ).



**Figure 4-2** The effect of turbidity on the irreversible fouling rate of the MF membrane (40 LMH, ferric sulphate dosed @ 0.5 mg/L as Fe<sup>3+</sup>, backwash every 30 minutes for 5 minutes, TMP corrected to 20°C)

**Table 4-7** Effect of coagulant on the fouling rate at different flux rates over a 7 day period

Flux	Ferric Sulphate Dose (mg Fe/l)	Reversible Fouling Factor (mbar/min. NTU)	Irreversible Fouling Rate (mbar/d)	Total Turbidity Load (NTU/m <sup>2</sup> )	Overall Permeability Decline ((l(m <sup>2</sup> hbar) <sup>-1</sup> ) <sup>-1</sup> )
40LMH	0.0	0.6	6	1.60	72.8
	0.5	0.7	5	1.99	55.8
45LMH	0.5	0.3	12	2.89	115.5
	0.0	1.2	37	2.04	134.5
50LMH	0.5	0.4	9	3.10	120.7

Results (Table 4-7) show fouling rate for each one-week trial to increase with increasing flux, but to decrease with coagulant addition. In the absence of coagulant, fouling rates were greatly affected by the applied flux, with a doubling of reversible fouling factor and a six-fold increase in the irreversible fouling rate on increasing the flux from 40 to 50 LMH. However, on dosing with coagulant the reversible fouling factor decreased by 50% and the irreversible fouling increased by only 50% when compared with the corresponding rates

recorded at 40LMH without coagulant - despite a 50% higher turbidity load during the coagulant trial. Results demonstrate a beneficial impact on reversible and irreversible fouling from the use of coagulant at doses as low as 0.5 mg/L as  $\text{Fe}^{3+}$ , significantly below doses employed in reference installations (Table 4-2) and corroborating previous findings (Choi and Dempsey, 2004) where coagulant doses insufficient to affect organic matter removal were nonetheless found to reduce fouling.

The irreversible fouling rates quoted in Table 4-7 demonstrate that, for operation between 0.2 and 0.8 bar transmembrane pressure (TMP), an interval of 21 days can be easily maintained in all cases except 50 LMH without coagulant. At 50 LMH without coagulant, a chemical cleaning interval of only 14 days is implied. However trials have shown that this can only be achieved if the turbidity is maintained below 5 NTU, which is not practical. Even a small increase in turbidity, for example an increase to 8 NTU over 12 hours, was found to be sufficient to cause a rapid increase in the irreversible fouling rate which, combined with the increased fouling rate at this flux, caused the plant to shut down for chemical cleaning. In contrast, at 50 LMH with coagulant the pilot plant could handle turbidity spikes up to 22 NTU over 12 hours without permanent changes in fouling rate. The use of coagulant thus enables the pilot plant to operate sustainably at higher fluxes with fouling rates associated with operation at lower fluxes.

### **4.3.3 Cost Analysis**

Results suggest that the flux rate can be increased by 25%, allowing a 20% reduction in membrane area and a commensurate reduction in capital expenditure (CAPEX) through membrane and tankage costs and reduced footprint (Figure 4-3). Coagulant dosing, however, impacts negatively on CAPEX through installation of a coagulant dosing pump, chemical storage and a control system. If these two CAPEX elements are assumed roughly equal then the cost benefit provided by coagulant dosing and higher-flux operation is approximated by the reduced cost of membrane replacement vs. the cost of adding coagulant over the life of the membrane.

An outline cost analysis thus proceeds through a consideration of the projected coagulant cost per kg of coagulant ( $L_c$ ) and the cost per  $m^2$  of the membrane ( $L_m$ ). The OPEX in  $\text{p/m}^3$  permeate associated with these two components are respectively given by  $L_m(1/J_1 - 1/J_2)/t$  and  $c L_c$ , where  $t$  is the membrane life and  $c$  the dose in coagulant mass per  $m^3$ . Even with a conservative assumptions of a coagulant cost of  $\text{£}500/\text{tonne}$  as Fe projected to increase at 8% p.a. coupled with a projected constant membrane replacement cost of  $\text{£}17/m^2$ , based on current costs, pre-coagulation at a dose of 0.5 mg/L Fe provides a cost benefit for a membrane life up to 14 years provided the 25% increase in flux is sustained. Based on a realistic membrane life estimate of seven years, the cost benefit of coagulant dosing is around 0.10  $\text{p/m}^3$  treated water. This is to be distinguished from the much higher doses employed by previous workers (Table 4-1 and Table 4-2) of between 2 (Fan et al., 2008, Choi and Dempsey, 2004) and 15 mg/L (Bagga et al., 2008): for a 5 mg/L ferric dose and a cost penalty of 0.26  $\text{p/m}^3$  would result based on the same assumptions.

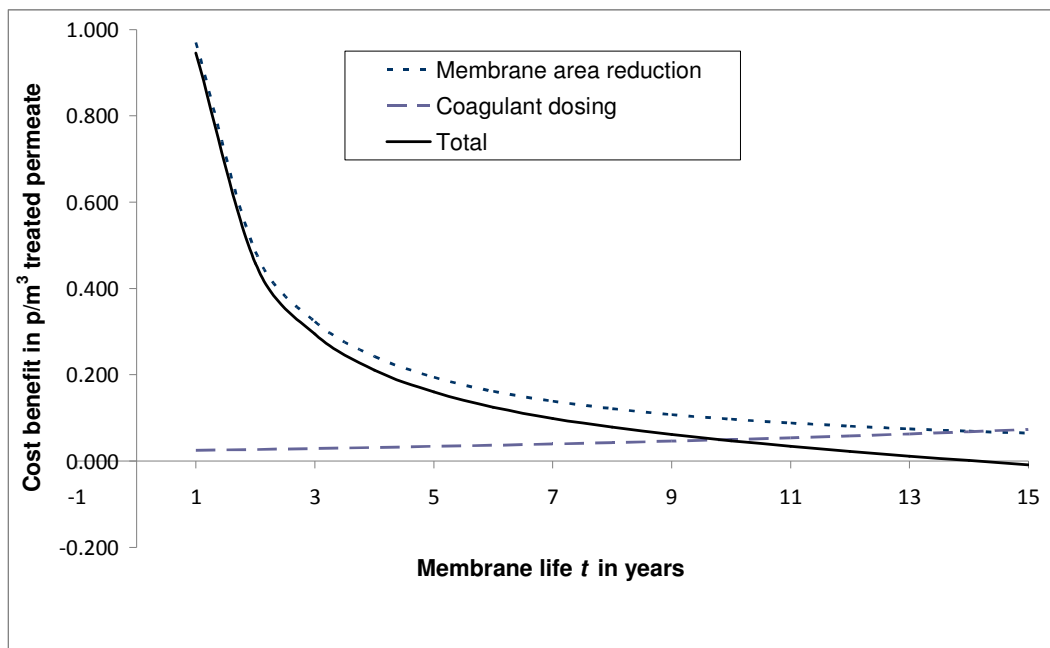


Figure 4-3 Cost benefit of pre-coagulation at 0.5 mg/L

## 4.4 Conclusions

The technical and cost benefit of using coagulant at the low doses associated with charge neutralisation, rather than higher doses for sweep flocculation, have been demonstrated at pilot scale. Pilot scale tests of ferric chloride, whose efficacy had been identified from bench-scale jar testing and scoping pilot trials, revealed it to provide sufficiently robust fouling amelioration during turbidity spikes.

In the absence of coagulant addition an increased flux from 40 LMH to 50 LMH produced a disproportionate increase in fouling rate, exacerbated by small increases in turbidity and leads to unsustainable operating conditions.

Employing coagulant dosing of 0.5 mg/L as Fe at 50 LMH reduced both the reversible and irreversible fouling to similar levels to those observed for optimised operating conditions without coagulant at 40 LMH.

The coagulant dose required to influence fouling rate was only a fraction of that required to obtain significantly enhanced organic matter removal. Fouling amelioration appraisal based on organic matter removal measured from jar testing thus appears to greatly over-estimate the coagulant dose required for fouling reduction, corroborating previous reports.

The cost benefit offered by dosing at this concentration to sustain a 25% higher flux exceeds 0.1 p/m<sup>3</sup> based on a membrane life of seven years. Moreover, in practice coagulant dosing would be required only during periods of high turbidity loads, reducing the overall coagulant consumption and further increasing the cost benefit.

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## **CHAPTER 5: Powdered activated carbon- microfiltration for wastewater reuse**

Hatt, J.W., Germain, E. and Judd, S.J., (2012) Powdered activated carbon – microfiltration for wastewater potable reuse, in press in *Separation Science and Technology*



## 5.1 Introduction

Membrane fouling by natural organic matter (NOM) remains a key issue in the application of membrane filtration technology to water treatment, with much research generated. Early studies (Wiesner et al., 1989) revealed colloidal matter to significantly contribute to microfiltration (MF)/ultrafiltration (UF) membrane fouling; coagulants have been shown to aggregate particles to promote their rejection by the membrane. Coagulation have been proven effective in removing aromatic NOM species of high molecular weight (MW) and hydrophobicity, characterised by a specific ultraviolet absorbance (SUVA) value above 4 L/(mg.m) (Edzwald and Van Benschoten, 1990), as well as those high MW compounds such as proteins and polysaccharide (Amy, 2008), which otherwise foul the membrane. However, there are cases where the use of coagulant has resulted in increased fouling demonstrating the requirement for onsite testing (Karimi et al., 1999, Schäfer et al., 2001). Other work (Fan et al., 2001, Dong et al., 2007) indicates hydrophilic neutral (HPN) organic matter, present in municipal wastewaters and associated with low SUVA values ( $\leq 2$  L/(mg.m)) and poor removal by coagulation, also generate fouling.

An alternative to coagulation for organic matter removal is activated carbon (AC), originally shown to remove organic material of wider molecular weight (MW) range ( $0.5 \times 10^2 - 10^9$  amu) than coagulation ( $0.5 \times 10^8 - 10^9$  amu) (Levine et al., 1985). Whilst evidence suggests that PAC (powdered AC) can remove significantly more of the organic matter than coagulant, it is the latter which appears to be more effective in suppressing membrane fouling, as demonstrated in laboratory studies (Shon et al., 2004) which revealed the coagulant to selectively remove the HPN and large MW organics. Against this, significant differences in both adsorption capacity and membrane fouling amelioration across three different PACs tested have been reported (Lee et al., 2005). A review of pilot plant experience of PAC:MF systems (Table 5-1) reveals wide variations in fouling, as manifested by the rate of increase in transmembrane pressure (TMP), across studies of waters of similar quality with reference to alkalinity and turbidity. This reflects the impact of both PAC

material and system hydrodynamics, with crossflow operation (ID 1 and 2) providing high scouring rates and commensurately high fluxes (Adham et al., 1991, Jacangelo et al., 1995) compared with dead-end mode operation (Farahbakhsh and Smith, 2002) where PAC usage resulted in increased TMP at similar flux rates.

The application of PAC to pilot-scale immersed MF/UF membrane systems is much less widely reported than crossflow systems, and produced conflicting results: both reduced (Best et al., 1999, Zhang et al., 2011) and increased (Farahbakhsh and Smith, 2002, Dialynas and Diamadopoulos, 2008, Huey et al., 1999) fouling over that associated with no PAC dosing has been reported. PAC dosing generally increases TOC removal, though the percentage increase does not relate to dose applied when comparing results across five studies. Such anomalies may arise from differences in membrane aeration, which has been shown to significantly influence organic carbon (OC) removal in immersed systems. Agitation by aeration apparently limits the extent of the PAC cake layer formed on the membrane, this layer being influential in rejecting TOC (Schideman et al., 2002). Results from a crossflow system have shown the application of PAC to reduce the quantity of organic matter deposited on hollow fibres by approximately 50% (Oh et al., 2006). The dosing protocol has also been shown to be influential: work by Campos et al (Campos et al., 2000) revealed that adding the entire PAC dose at the beginning of filtration cycle as a pulse input was more than twice as efficient in terms of DOC removal compared to continuous addition through inline dosing.

In recent years studies of PAC dosing in membrane systems has focused on either PAC particle size impacts (Lohwacharin et al., 2010, Matsui et al., 2009) or, for wastewater, dosing of membrane bioreactors (Yang et al., 2010, Guo et al., 2008), rather than as pretreatment upstream of UF/MF. Whilst PAC pretreatment has been found by some (Shon et al., 2004) to be less effective than precoagulation for fouling suppression, there remains an interest in assessing its efficacy for combined organics removal and membrane fouling suppression (through removal of high MW organics and HPNs). This is

particularly so in indirect potable reuse (IPR) schemes, which are of increasing importance worldwide and are generally based on a dual stage microfiltration/ultrafiltration (MF/UF) – reverse osmosis (RO) process for recovering secondary municipal wastewater. In such schemes, improved efficacy of the MF/UF stage in terms of removal of both organic matter and multivalent metals may be expected to either improve downstream RO performance (by fouling amelioration) or generally improved UF permeate product water quality.

This paper assesses the efficacy of a range of PACs for TOC removal (as determined from bench-scale tests) and reducing MF fouling (determined at pilot scale) with reference secondary municipal effluent and in the context of indirect potable reuse.

**Table 5-1 Summary of studies of the impact of adsorption on MF membrane reversible and irreversible fouling**

ID	Reference	Membrane	Raw water source and quality	PAC	Backwash details	Observation
1	Adham et al (1991)	Al Aquasource through lumens inside to out (i-o), cross-flow (cf)	flow Groundwater (pH 7.5, TOC 2.9 mg/L)	Calgon Corporation (coal based)	Not given	Low doses of up to 30 mg/L reduced fouling enabling either significantly longer filtration cycle (Adham et al) or increased flux rates from 100 to 136 LMH (Jacangelo et al). Adham et al also found TOC removal to increase from 5-10 % to 45% and TMP to decrease further with PAC doses up to 200 mg/L. Campinas and Rosa found 10 mg/L PAC to increase removal of tannic acid by 30%, humic acid by 13% and assimilable organic matter by 20%.
2	Jacangelo et al (1995)	Delta Water (pH 7.9, 72 mg CaCO <sub>3</sub> /L, in TOC 5.2 mg/L and 12 NTU); PAC recirculation loop, River Water (pH 7.6, 20 mg CaCO <sub>3</sub> /L, 100 kDa TOC 7.4 mg/L and 1.4 NTU)			Reverse every 30 mins	flow
3	Campinas and Rosa (2010)	molecular weight cut-off (MWCO) Max. pressure (P) 200 kPa, 0.93 mm inside diameter (id)	Commercial humic & tannic acid and Norit SA-JF algal organic matter (AOM).	Norit SA-JF	Short lab-scale experiments so no backwashing	
4	Huey et al (1999)	Canal water inside diameter (id)	Canal water TOC 2.3 mg/L, 0.5 – 16 NTU	Norit Hydrocarco Type O.	Reverse every 20 mins	At 10 mg/L maintained 100-115 LMH for 28 d period which decreased on increasing dose to 20 mg/L. TOC removal decreased from 12 to 7% with PAC; UV absorbance removal increased from 11 – 18%.
5	Farahbakhsh and Smith (2002)	As above but dead-end operated	but River water dead-end pH 5.8 – 6.9, low alkalinity, TOC 2.43 mg/L, 0.55 NTU	Calgon Corporation (coal based)	Air pulse reverse plus rinse every 30 mins	in At 115LMH, TMP increased with PAC addition of 5-18 to zero PAC. TOC removal decreased slightly from 11 – 10% with PAC but UV absorbance removal increased from 11 – 18%.
6	Huey et al (1999)	Memcor dead-end, nominal pore size 0.2 µm; max P= 200 kPa, 0.3 mm lumen id	(o-i), Canal water TOC 2.3 mg/L, ≤0.4 NTU	Norit Hydrocarco Type O.	Air enhanced backwash rinse every mins;	Dose of 10 and 20 mg/L at 75-90 LMH significantly plus increased frequency of chemical cleaning compared to zero PAC. TOC removal decreased slightly from 11 – 10% with PAC but UV absorbance removal increased from 11 – 18%.
7	Best et al (1999)	Zeeweed Lime softened, dead-end, water nominal pore size 0.04 µm or 100-120 kDa, aerated)	settled water for drinking water (allowed to build up)		Not given	25 mg/L dose significantly reduced fouling at 76 LMH compared with no PAC, enabling flux increase to 100 LMH. Also improved removal of TOC and UV abs.
8	Farahbakhsh and Smith (2002)	River water pH 5.8 – 6.9, low alkalinity, TOC 2.43 mg/L, 0.55 NTU		Calgon Corporation (coal based)	Reverse flow for PAC addition every 15 mins	for PAC addition (0 – 20 mg/L) at flux of 50 – 100 LMH. No increase in TOC or UVA removal with the addition of PAC.
9	Dialynas and Diamadopoulos (2008)	Wastewater effluent	Wastewater effluent 2.3 L/min, TOC 7.4 mg/L, 3.4 NTU	Eurocarb, (coconut based)	Reverse flow for PAC addition every 15 mins	for Rapid rise in TMP with 2.5 g/L PAC but DOC removal increased from 25 to 60%; TMP stable with 0.75 g/L GAC but DOC removal only increased to 36%.
10	Zhang et al (2011)	Algal rich water (dead-end; nominal pore size 0.01 µm; aerated)	Algal rich water (TOC 1.0 – 2.4 mg/L, 0.016 – 0.020 cm <sup>1</sup> )	coconut	Short lab-scale experiments so no backwashing	4 g/L dose reduced TMP increase over 15 days by so 30% and increased removal of UV abs by 27% & of DOC by 11%



## 5.2 Materials and methods

### 5.2.1 Bench-scale tests

Preliminary jar tests were carried out to assess the adsorptive capacity of six different PAC materials (Table 5-2) at doses up to 400 mg/L for UV<sub>254nm</sub>, UV<sub>400nm</sub> and dissolved organic matter (DOC). AC carbon samples were ground to such that all the sample passed through a US 325-mesh (44 µm) sieve to ensure that 90% adsorption capacity was attained within the 2 h test period, in accordance with standard methods (ASTM, 1998). Triplicate tests were conducted using six 500 mL amber glass bottles with PTFE coated lids, following standard protocols (ASTM, 1998). All isotherms were conducted at 10 and 20 °C temperature without chloramines addition and 20 °C with chloramine addition. A magnetic stirrer plate was used to suspend the AC for the 2 hour test period. Further 2-hour batch tests were conducted at two different PAC doses (50 and 200 mg/L) with constant mixing at 20 °C to assess adsorption kinetics. Extracted samples were filtered through a 0.45 µm filter paper and the filtrate immediately analysed.

**Table 5-2 PAC characteristics, volumes in mL/g**

Supplier	PAC	Base material	Micropore volume	Mesopore volume	Macropore volume	Total pore volume
Supplier A	PAC A	coconut	0.33	0.11	0.17	0.62
Supplier B	PAC B	coconut	0.37	0.12	0.19	0.68
Supplier B	PAC C	wood	0.19	0.37	1.68	2.24
Supplier C	PAC D	coal	0.30	0.19	0.26	0.75
Supplier C	PAC E	coal	0.30	0.20	0.26	0.76
Supplier D	PAC F	coal	0.35	0.33	0.20	0.88

Hydrophobic and hydrophilic fractions were determined through fractionation using XAD resin adsorption techniques according to a previously reported method (Goslan et al., 2004); water samples were fractionated following pretreatment with 200 mg/L of each PAC for 30 mins.

### 5.2.2 Pilot plant

The 600 m<sup>3</sup>/d pilot plant has been described elsewhere (Raffin et al., 2011b), and comprised 16 immersed microfiltration (MF) membrane modules (Siemens

Memcor CMF-S 0.04 µm). The plant receives secondary effluent (Table 5-3) from a conventional activated sludge municipal wastewater treatment works in north London, UK. It comprises a 500 µm-rated automatically backflushed filter (Bollfilter model 6.18) upstream of the MF skid, the permeate then being fed to a reverse osmosis (RO) unit (Hydranautics ESPA-2) and/or a hydrogen peroxide-UV advanced oxidation process (AOP).

PAC was added to the membrane tank as a single dose, reported as being more effective than continuous dosing (Campos et al., 2000), at the start of each six-hour trial. The selected dose was equivalent to a continuous dose of 5 or 25 mg/L. Each carbon dose was mixed with sufficient water to form a slurry and added to the tank during refilling to ensure complete mixing. Each test was duplicated on a different day to assess reproducibility. Membrane integrity was ensured through pressure decay tests conducted before and after each period of PAC dosing.

**Table 5-3 Feed water quality parameters, Apr 2011-Jan 2012**

	Mean	Standard deviation
Turbidity (NTU)	9.8	17.3 (118%)
TOC (mg/L)	7.5	1.8 (24%)
pH	7.0	0.4 (6%)
Temperature (°C)	18.4	2.5 (14%)
Alkalinity (mg/L CaCO <sub>3</sub> ) *	304	21.6 (7%)
TSS (mg/L) *	9.64	4.74 (49%)

All from continuous online monitoring other than \*based on periodic spot sampling

Initial tests were carried out at a flux of 40 L/(m<sup>2</sup>h) (LMH), which previous work (Raffin et al., 2011b) revealed to be the highest flux that could be sustained over a range of influent conditions and with chemical cleaning at 21-day intervals without chemical pre-treatment. Tests were repeated at 50 LMH to assess permeability sustainability at this higher flux through PAC pretreatment.

MF backflushing was every 30 minutes, or else triggered at a TMP of 78 kPa, for 2 minutes with air and water at a flux of 45 LMH. During testing, the membranes were chemically cleaned at least weekly. Membrane chemical

cleaning was with 540 mg/L sodium hypochlorite at 30°C. Data were recorded on a supervisory control and data acquisition (SCADA) system. Online instrumentation for the MF included Siemens *Magflow 6000* flowmeters on the feed and permeate lines, Hach Lange turbidity meters on the feed and permeate lines, and ABB pH and temperature monitoring on the discharge. Samples taken before (pre PAC addition) and after the MF were analysed on site for TOC, UV<sub>254nm</sub> and UV<sub>400nm</sub> and at the Thames Water Laboratory for metals and other inorganic compounds using standard methods.

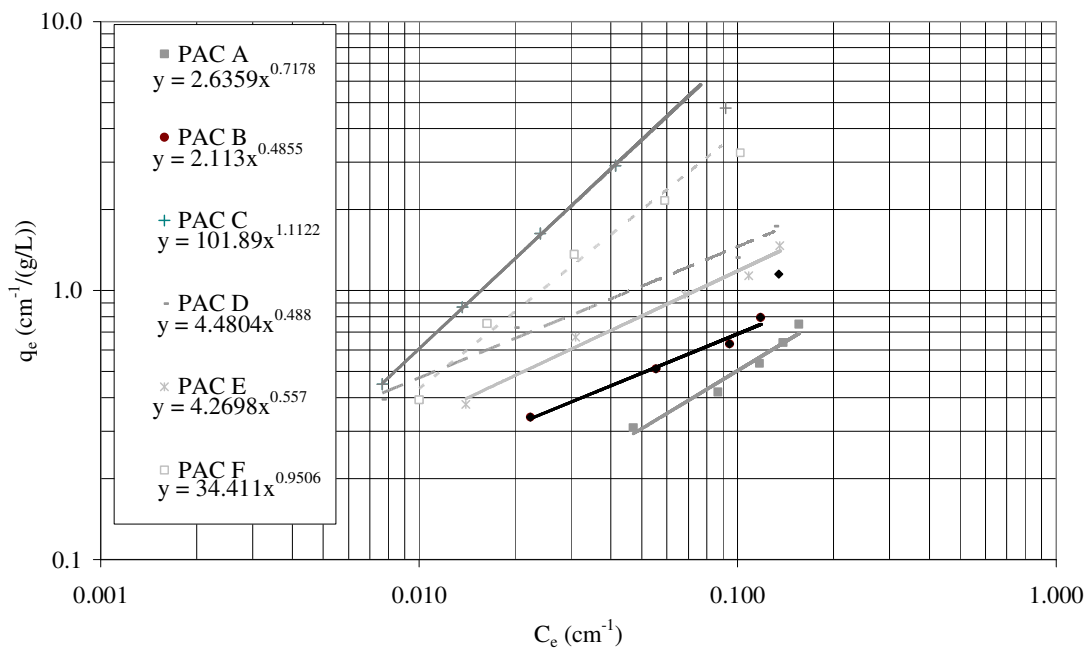
## 5.3 Results and discussion

### 5.3.1 Jar tests

Figure 5-1 shows the UV<sub>254nm</sub> adsorption isotherm for organic removal at 20 °C for the 6 different PACs. The Freundlich model ( $q_e = K C_e^{1/n}$ ) was applied to the adsorption data,  $q_e$  and  $C_e$  being the equilibrium surface and liquid concentrations respectively, and  $K$  and  $1/n$  respectively relating ostensibly to the adsorbate capacity and the adsorption strength.

Similar isotherms were produced for organic removal measured as either TOC or UV<sub>400nm</sub> (representing colour). For the colour adsorption isotherms, the data set for each PAC showed two distinct zones: a strongly adsorbable zone represented by an almost vertical line and a moderately adsorbable zone. The isotherm was fitted only to the data in the latter zone; applying the isotherm to the low concentrations in the highly adsorbable zone is known to significantly underestimate adsorptive capacity (Frick and Sontheimer, 1983). In the case of PAC A, all data were in the highly adsorbable zone: no isotherm could be fitted to these data, and the material had a lower capacity for colour compared to the other PACs.  $R^2$  values ranged from 0.83 to 1.00, 83% of the values being between 0.90 and 1.00 and the average being 0.90, confirming the good fit of data to the Freundlich isotherm. PAC C and F demonstrated higher adsorption capacity for the aromatic and chromophore-containing organics (i.e. UV<sub>254nm</sub> and UV<sub>400nm</sub>).

According to the adsorption data for all three water quality determinants (Table 5-4), there are wide differences in capacity according to the determinant used. From the PACs tested the adsorption capacity  $K$  measured as  $UV_{254nm}$  or  $UV_{400nm}$  varied with base material and was of the order wood > coal > coconut, attributable to the variation in AC pore volume across base material type. The coal and wood based PACs had mesopore volume in the range 0.32-0.37  $cm^3/g$ , more than double that of the coconut based PACs (0.11- 0.12  $cm^3/g$ ). The wood-based PAC had a very high macropore volume, explaining its improved capacity for higher MW compounds and corroborating the findings of Lee et al (1981). At high concentrations, the adsorption capacity for organic matter measured as TOC (mg/L) followed the same trend as for  $UV_{254nm}$  or  $UV_{400nm}$ . However, at lower levels, the coal-based materials provided higher  $K$  values than the wood-based ones, suggesting the former to have a higher capacity for non-aromatic organic compounds. Results contradict those of Lee et al (2005) who tested three different PACs on wastewater and found the coconut-based PAC to outperform the wood-based and then the coal-based materials with reference to TOC removal.



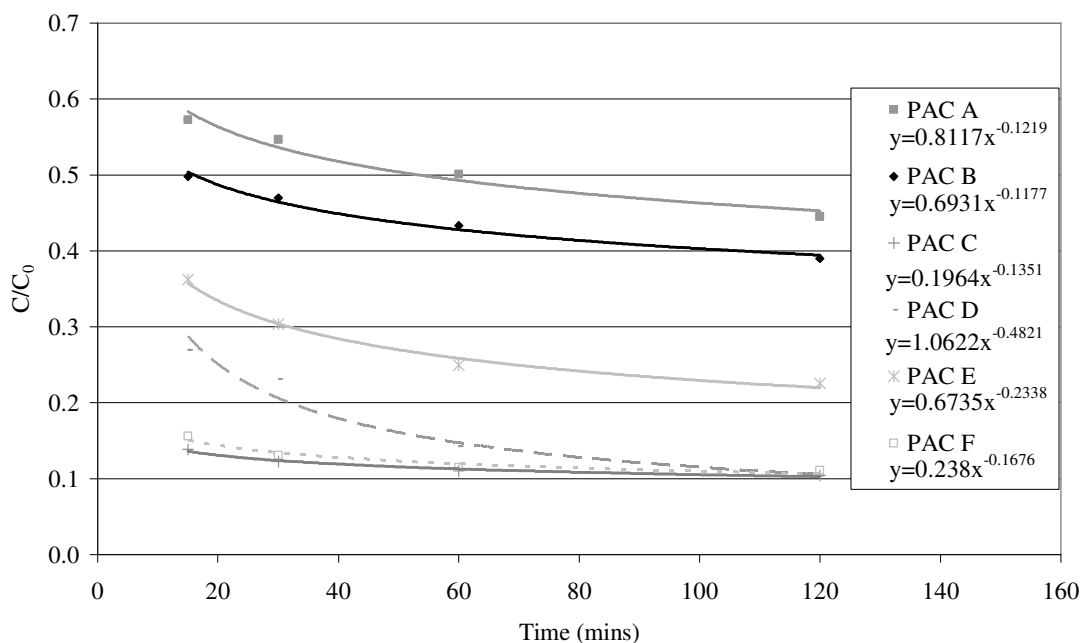
**Figure 5-1 Freundlich adsorption isotherm for all PAC materials, based on  $UV_{254nm}$  removal**

**Table 5-4 Isotherm parameters**

	TOC (mg/L)		UV <sub>254nm</sub> (cm <sup>-1</sup> )		UV <sub>400nm</sub> (mg/L)	
	K	1/n	K	1/n	K	1/n
PAC A	3.5	0.85	2.6	0.72	nm	nm
PAC B	7.5	0.63	2.1	0.49	50.4	0.11
PAC C	3.5	2.08	101.9	1.11	546.6	0.47
PAC D	13.5	0.61	4.5	0.49	162.2	0.15
PAC E	11.0	0.67	4.3	0.56	39.4	0.56
PAC F	14.4	0.95	34.4	0.95	253.4	0.39

Since adsorbate solubility and mass transfer by diffusion may be affected by temperature, and so adsorption rate, jar tests were repeated at 10 °C - the minimum temperature normally encountered for this secondary effluent. Statistical analysis using the paired student t-test on the organic removal rates for each PAC showed a temperature decrease of 10 °C provided a statistically significant difference in adsorption capacity for four out of the six PACs tested. For *PACs A and F* TOC removal was reduced by ~50 % whilst for *PAC E* it increased by 8 %, the change in TOC removal increasing with decreasing concentration in each case. However, there was no difference in UV<sub>254nm</sub> or UV<sub>400nm</sub> removal, suggesting that only non-aromatics were affected. For *PAC D*, decreasing temperature did not affect TOC removal but increased UV<sub>254nm</sub> removal by 8.5% and UV<sub>400nm</sub> removal by 54%, suggesting that in this case aromatics solubility was influenced by temperature. The significant impact of temperature on organic removal implies that the required dose rate for four of these PACs would be temperature dependent.

As expected from the adsorption isotherms, *PAC C* and *F* showed the highest removal rates over the test period (Figure 5-2). An 86% UV<sub>254nm</sub> removal was attained after just 30 mins, increasing to 90 % after two hours, whereas for *PAC D* only 73% adsorption was recorded after 30 mins before increasing to 90 % over the same period. Similar results were obtained for TOC and UV<sub>400nm</sub> removal. These results corroborate those of Najm et al. (1998) and Campos et al. (2000) who also found adsorption to be rapid for first 30 mins before slowing, attributing this to the variation in diffusion rates between high and low MW compounds.



**Figure 5-2 Kinetics of UV254nm Removal**

### 5.3.2 Molecular characterisation

Results of the XAD resin fractionation (Table 5-5) show that, with the exception of the coconut-based PACs, all PAC materials preferentially removed adsorbates according to the priority sequence hydrophobic > hydrophilic acid (HPA) > HPN fraction. However, the percentage removal of each fraction varied widely between each material. *PAC C* and *F* removed the greatest percentage of the hydrophobic and HPA fractions, whereas *PAC D* and *F* removed the greatest percentage of the hydrophilic neutral fraction. Therefore, based on the findings of Fan et al (2001) and corroborated by Dong et al (2007) whereby membrane fouling was reported to be predominantly caused by a combination of hydrophobic and HPN fractions, *PAC F* would be expected to provide the most membrane fouling suppression of those PACs tested.

**Table 5-5 Effect of dosing with 200 mg/L of PAC for 30 mins on each organic fraction, measured as mg/L TOC (percentage removal)**

	Secondary effluent	PAC A	PAC B	PAC C	PAC D	PAC E	PAC F
Hydrophobic fraction	2.85	2.61 (8.6)	2.02 (29.1)	0.80 (71.8)	1.32 (53.5)	1.27 (55.3)	0.92 (67.8)
Hydrophilic acid (HPA) fraction	2.11	2.15 (-2.3)	1.77 (15.9)	0.88 (58.4)	1.23 (41.8)	1.16 (44.7)	0.82 (60.9)
Hydrophilic neutral (HPN) fraction	6.80	4.67 (31.3)	5.03 (26.0)	4.50 (33.8)	4.06 (40.2)	4.78 (29.7)	3.97 (41.6)
Total (mg/L)	11.75	9.43 (19.8)	8.82 (24.9)	6.18 (56.3)	6.61 (43.7)	7.22 (38.6)	5.71 (51.4)

### 5.3.3 Pilot test results

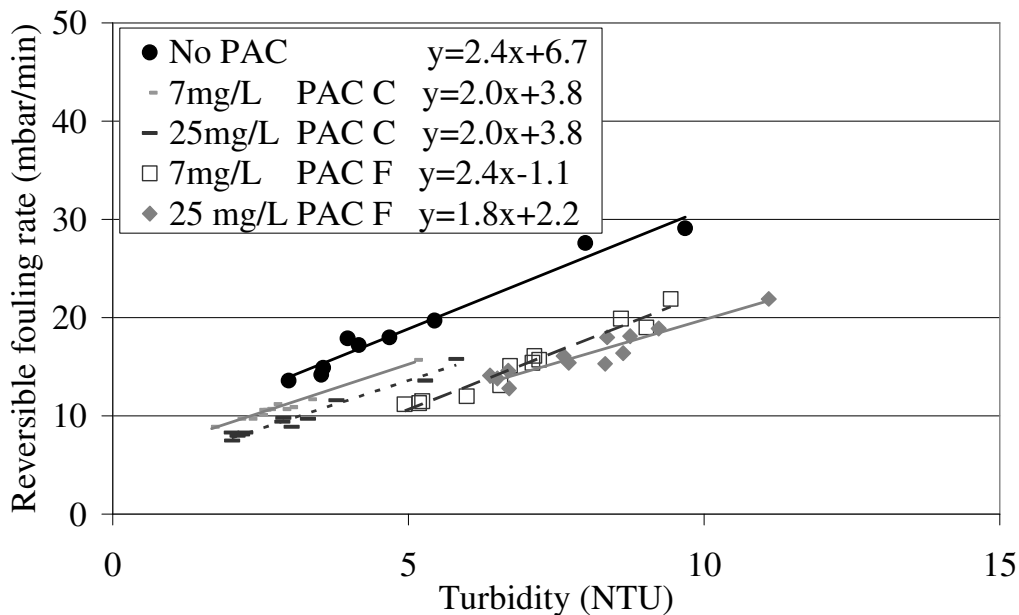
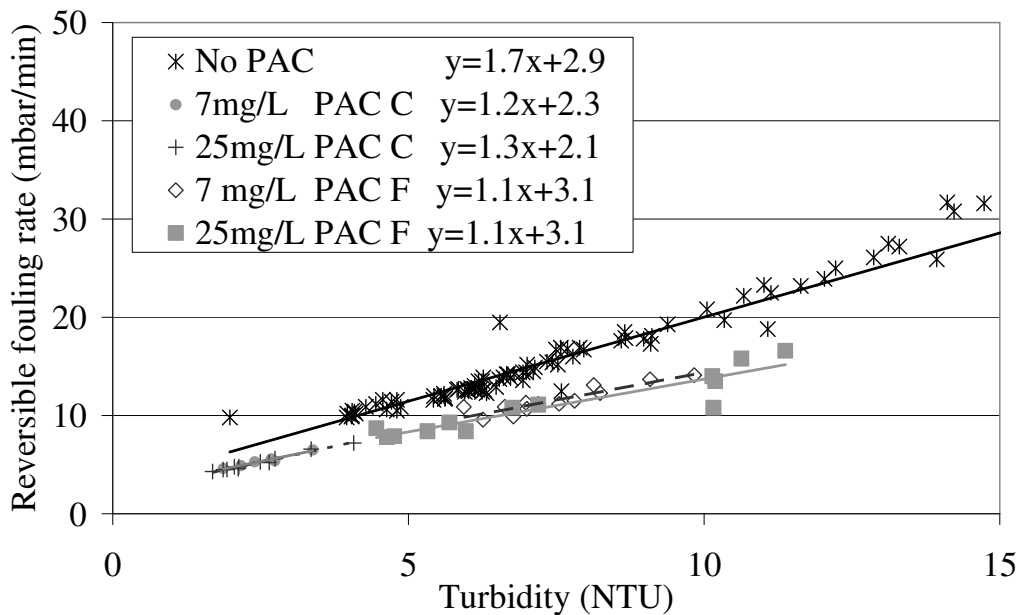
From the equilibrium and kinetic jar test studies, *PAC C* and *F* were chosen as the best adsorbents for the PAC/MF hybrid process. Trials were conducted to assess the effect of PAC addition on the reversible (that which is removable by hydraulic cleaning) and irreversible (that which is removable by chemical cleaning) fouling rates.

As expected from previous work (Hatt et al., 2011), trials conducted with both PACs at both doses and flux rates, with backflushing every 30 minutes, revealed a linear relationship between reversible fouling rate (rate of change in TMP during a filtration cycle) and turbidity (Figure 5-3). Whereas the intercept of the plots shown in Figure 5-3 reflect the initial fouled state of the membrane, the slope of the plots (i.e. the reversible fouling factor) is indicative of the fouling propensity of the cake. Figure 5-3a shows that at 40LMH fouling decreases with PAC (17-35%) but that the dose does not impact on the reversible fouling rate trend with feedwater turbidity, nor the absolute value. At 50 LMH (Figure 5-3b) the slope changes little with dose, as with the 40 LMH data, although the slope is greater because of the increased flux (as reflected in the respective zero-PAC lines). Xia et al (2007) and Tomaszewska and Mozia (2002) also found that the effect of PAC on fouling reduction was independent on dose. It thus appears that the cake thickness and/or overall permeability is unaffected by suspended particle concentration. However, at 50 LMH the absolute fouling rate

value appears to decrease slightly with increase PAC dose at the higher flux. Although work by others (Jacangelo et al., 1995, Farahbakhsh and Smith, 2002, Huey et al., 1999) has investigated the effect of PAC at varying doses and fluxes, insufficient data has been published on the change of TMP per filtration cycle for each combination of PAC dose and flux to enable a comparison with their results. Whilst the figures generally indicate reduced fouling, the reduction is insufficient to extend the filtration cycle. To extend the filtration cycle to 45 mins would require the fouling rate to be < 12 mbar/min respectively which as can be seen from Figure 5-3a requires the turbidity to be <8 NTU which although this is more attainable than without PAC when the turbidity needs to be less than 5 NTU, it is still less than the average value for turbidity of 9.8 NTU experienced by the plant (Table 5-3).

The difference between the two PACs was more apparent for irreversible fouling data (Figure 5-4). PAC C clearly reduced irreversible fouling, demonstrated by the increased permeability at both fluxes, with the largest dose producing the greatest impact. For PAC F, however, the permeability decline increased significantly at both fluxes and doses, despite its superior HPN and hydrophobic organics adsorption - considered to be the main fouling proponents. This difference between the two PACs could be attributed to density differences. PAC C, being wood based, had a significantly lower density than the coal-based PAC F. This material would thus be expected to be retained in suspension more readily and so be available to scour the membranes, whereas the PAC F is more likely to settle out in the membrane tank. However, organic removal figures are in reasonable agreement with those obtained at bench scale suggesting that mixing was not a limitation. Although it is possible that PAC F accumulated on the membrane surface to a greater degree, was this to be the case it might also be expected for the reversible fouling to have increase as well for this PAC.

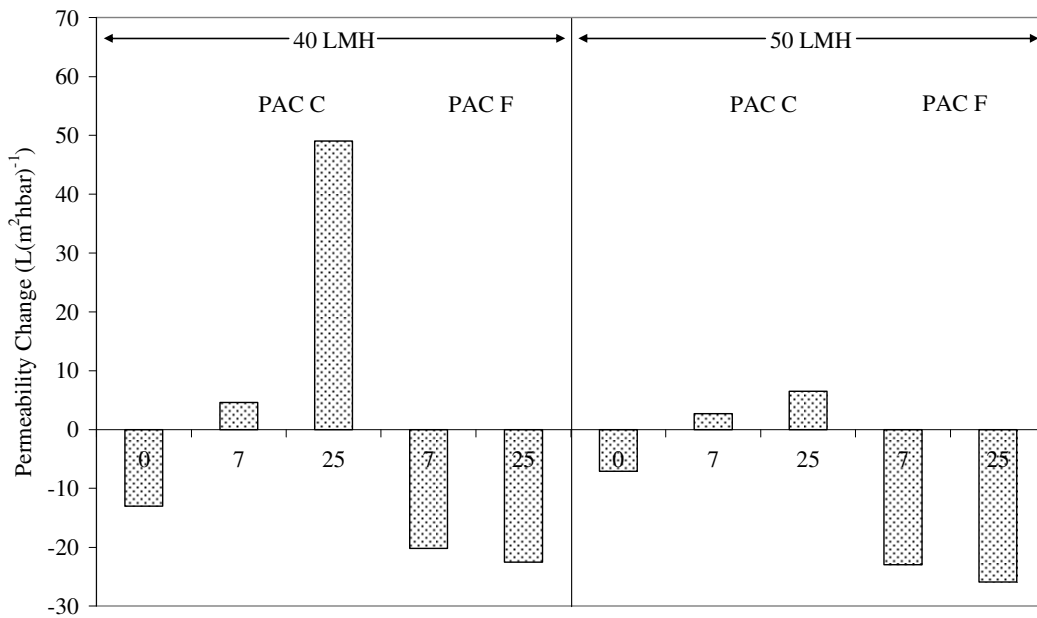




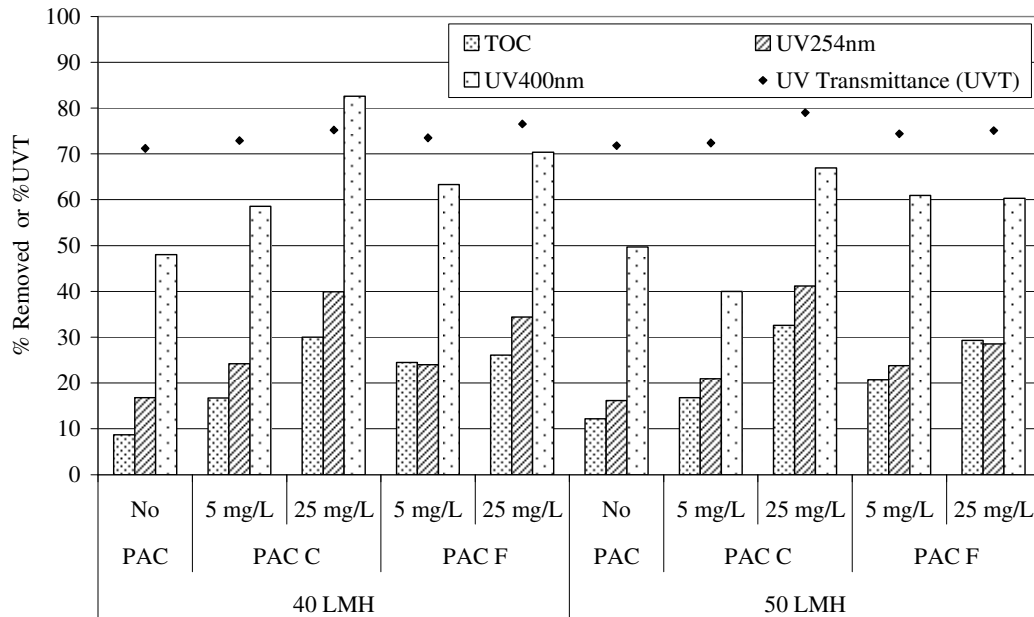
**Figure 5-3 Effect of PAC type and dose on reversible fouling factor, represented by gradient, at a) 40 LMH and b) 50LMH**

As expected from the isotherm data, PAC addition significantly increased organic removal over that from using MF alone, especially at the higher PAC dose (Figure 5-5). This is in contrast to the results from previous work (Table 5-1) where those systems using aeration for mixing resulted in poor organics

removal and suggested aeration to be detrimental to organic removal (Schideman et al., 2002). Removal rates were also found to be time dependent: whereas equilibration trials indicated increased adsorption with time (Figure 5-2), the pilot plant filtration trials showed decreased removal over the course of the 30 minute filtration cycle due to exhaustion of the PAC by the feedwater passing through it in the membrane tank. Removal decreased by 5-10% from initial levels of 20-25% over a 10 minute period of the filtration cycle. This compares less favourably with the results reported by Campos et al (2000), who recorded removal efficiencies decreasing by 15% from initial values of 50-75% over the first 20 minutes of the cycle at a the higher PAC dose of 40 mg/L. The bench scale isotherm tests revealed the performance of PAC C was more dependent on initial DOC concentration than PAC F, providing a commensurately higher  $1/n$  value. It would thus be expected for organic removal to decrease more rapidly with filtration cycle time for the PAC C than for the PAC F.



**Figure 5-4 Effect of PAC grade and dose on irreversible fouling, as represented by permeability change.**



**Figure 5-5 Effect of PAC addition on percentage removal of organics (as measured as TOC, UV400nm and UV254nm) and UV transmittance (where UV Transmittance =  $100 \times 10^{-UV_{254nm}}$ ).**

Results of the pressure decay tests remained constant throughout the test period demonstrating that complete membrane integrity was maintained.

## 5.4 Conclusions

The adsorption capacity and kinetics of six different PACs were determined from laboratory scale adsorption studies using the Freundlich isotherm to fit the data. The adsorption capacity  $K$  measured as  $UV_{254nm}$  or  $UV_{400nm}$  and at high concentrations for TOC, varied with base material and was of the order wood > coal > coconut. *PAC C* and *F* proved to have the greatest adsorption capacity and the fastest kinetics, attaining 86% organic removal within 30 minutes.

With the exception of *PAC B* and *C*, temperature had a significant affect on the adsorption capacity; the size of the effect varied with concentration and the method of organic measurement. This highlights the need to test PAC over the full range of temperatures encountered in practice.

Based on the bench-scale results, *PAC C* & *F* were trialled at pilot plant scale at two different doses (5 and 25 mg/L) and fluxes (40 and 50 LMH) as pre-treatment to the MF. Both PACs produced a small reduction in reversible fouling which was independent of dose, though this reduction was insufficient to enable increased flux or decreased backwash frequency.

*PAC C* also demonstrated a significant reduction in the irreversible fouling rate, potentially enabling the MF operate for a longer periods between chemical cleaning and so reducing costs. Longer-term trials are required to confirm this and verify the effect of PAC on the life of the MF hollow fibres. *PAC C* and *F* both significantly improved the removal of organics, even at short time scales when applied to the immersed MF system at pilot scale.

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## **CHAPTER 6: Granular activated carbon for removal of organic matter and turbidity from secondary wastewater**

Hatt, J.W., Germain, E. and Judd, S.J., Granular activated carbon as pretreatment for microfiltration, in press in *Water Science and Technology*



## 6.1 Introduction

Membrane fouling by natural organic matter (NOM) remains a key issue in the application of membrane filtration technology to water treatment, with much research generated. Early studies (Wiesner et al., 1989) revealed the colloidal fraction of natural organic matter to contribute most significantly to fouling in microfiltration(MF)/ ultrafiltration(UF) membranes. Whilst it has been demonstrated that coagulants can aggregate particles so as to promote their rejection by the membrane rather than cause membrane pore plugging, it has been reported (Karimi et al., 1999, Schäfer et al., 2001) that application of coagulants has resulted in increased fouling.

An alternative to coagulants for removing organic matter is activated carbon (AC). Work by Levine (1985) originally demonstrated AC to remove organic material of wide ranging molecular weight (MW) ( $0.5 \times 10^2 - 10^9$  Da) compared to coagulation ( $0.5 \times 10^8 - 10^9$  Da). AC is available in granular (GAC) and powdered (PAC) form; PAC is added to the water to be filtered by the MF/UF membrane whereas GAC is used as a filtration media upstream of the membrane. Previous work (Hatt et al., in press) evaluated the addition of powdered activated carbon (PAC) within the membrane tank of the immersed membrane. Whilst this work demonstrated that PAC could reduce the organic content of the MF effluent, the effect on reversible fouling was insufficient to facilitate longer filtration times. Reversible fouling has been found to be strongly correlated to turbidity (Hatt et al., 2011), and the use of AC in the granular form within a fixed bed which has been reported to reduce turbidity by 50-95%, depending on the influent turbidity and empty bed contact time (EBCT), as well as removing organic matter (Table 6-1). GAC pretreatment has been shown to halve the rate of flux decline (Shon et al, (2004), and reduce the modified fouling index (MFI) by 91 % for dead-end microfiltration of wastewater (Khorshed et al., 2011). A 58 % reduction in MFI has been reported for filtering rainwater with a turbidity of 42 NTU and total suspended solids of 160 mg/L (Areerachakul et al., 2009), and an 88% reduction for seawater of <1 NTU

turbidity (Chinu et al., 2009) which then significantly reduced fouling of the downstream reverse osmosis membranes.

**Table 6-1 - GAC performance and operation, published studies of turbidity removal**

Reference	Raw water source and quality	Down-flow velocity (m/h)	EBCT (mins)	GAC	Trial duration (d)	Turbidity removal (%)	TOC removal (%)
Graese et al (1987)	Clarifier effluent (Iowa) (1.1 – 4 NTU)	6	7.5–9.4	CECA GAC 30 8 x 30	3 - 4	65-87.5	NA
	Clarifier effluent (Virginia) (2-5 NTU)	4.7	5.6–7.5	Calgon Filtrasorb 200 12 x 40	4	90	NA
	Clarifier effluent (Pennsylvania) (2-4 NTU)	7.2	6.3	Calgon Filtrasorb 200 12 x 40	4	95	NA
Tsujimoto et al (1998)	River Water (19 NTU, 2.4 mg/L)	10	6	1.2 mm dia.	700	50	21
Kim and Kang (2008)	River Water (1.6-4.7 mg/L)	4.6	9.8	Calgon F820 1 mm dia	90		50
Chinu et al (2009)	Seawater (0.4-1.6 NTU)	5	9.6	0.3 mm dia.		25-81	
		10	4.8			50-87.5	
Mohammed et al (2011)	Stormwater (1.5 NTU, 4.3-9 mg/L TOC)	0.12 0.25	375 96	0.3 – 2.38 mm dia.	40- 60	68 - 75	99

The concentration of organic matter in a typical secondary treated effluent is normally in the 6-10 mg/L range of total organic carbon (TOC). Previous work (Hatt et al., in press) established that a minimum PAC dose of 50 mg/L was required to reduce the TOC level by 25%, and that further reduction in TOC level by PAC dosing would be prohibitively expensive in terms of reagent demand. It was also apparent that the short filtration cycles (30 minutes maximum) at which the microfiltration (MF) unit operated meant that the full capacity of the PAC was not reached due to kinetic limitations.

The use of GAC pretreatment would be expected to be more effective in reducing organic fouling, provided the contact time is sufficient to allow

substantial adsorption to take place, and may also reduce biological fouling (Wend et al., 2003). GAC filters remove organics through developing a biofilm on their surface. This film breaks down readily available biodegradable organic matter, enhancing its removal and so suppressing biological fouling through restricting this food source for biofilms formed in downstream processes. Work by Wend et al (2003) found the use of GAC to halve the fouling layer thickness of downstream membranes and reduce cell counts 4-5 fold whilst enhancing TOC removal by up to 38%. The long retention times within the biofilm permit biodegradation of the more recalcitrant NOM fraction (Carlson and Silverstein, 1998).

This work assesses the efficacy of seven commercially-available GAC media for organic removal and turbidity reduction using bench scale adsorption studies and supplementary column trials. Whilst bench scale tests provide useful comparative information on organic removal they cannot easily account for removal through bioactivity, nor can they provide an estimate of bed life unless the capacity obtained by extrapolating the isotherm data to the initial value is a good approximation. Also, with the column trials higher adsorption capacities can be achieved as the carbon is mainly in equilibrium with the influent rather than the effluent concentration as in the case of PAC. Bench scale tests may nonetheless provide data for comparative carbon usage rates based on adsorption capacity across a range of tested media.

## **6.2 Materials and methods**

### **6.2.1 Raw water**

Experiments were conducted using secondary wastewater effluent from a conventional activated sludge municipal wastewater treatment works in north London, UK (Table 6-2), all tests being carried out on the same day as sample collection. Samples were collected in 2.5 L glass amber bottles with PTFE lined screw lids and stored at <5 °C for no more than four hours prior to bench scale tests.

**Table 6-2 Feed water quality parameters, April 2011 - Jan 2012**

Parameter	Mean	Standard deviation
Turbidity (NTU)	4.3	2.5 (58%)
TOC (mg/L)	7.5	1.8 (23%)
pH	7.0	0.4 (6%)
Temperature (°C)	18.4	2.5 (13%)
Alkalinity (mg/L CaCO <sub>3</sub> ) *	304	21.6 (7%)
TSS (mg/L) *	9.64	4.74 (49%)

All from continuous online monitoring other than \*based on periodic spot sampling

### 6.2.2 Bench-scale tests

Preliminary jar tests using media doses up to 400 mg/L were conducted to assess the comparative adsorptive capacity of seven different GAC materials (Table 3) for UV<sub>254nm</sub>, UV<sub>400nm</sub> and dissolved organic matter (DOC) at a controlled temperature of 20°C. AC carbon samples were ground to below a grade of US 325-mesh (44 µm) to ensure that 90% adsorption capacity was attained within the 2 h test period, in accordance with standard methods (ASTM, 1998). Triplicate tests were conducted using six 500 mL amber glass bottles with PTFE-coated lids, following standard protocols (ASTM, 1998). A magnetic stirrer plate was used to suspend the AC for the 2 hour test period. Extracted samples were filtered through a 0.45 µm filter paper and the filtrate immediately analysed.

**Table 6-3 GAC material characteristics**

Supplier	Grade	Mesh Size	Base material	Micropore volume	Mesopore volume	Macropore volume	Total pore volume
Supplier A	GAC 1	12 x 40	coconut	0.33	0.11	0.17	0.62
Supplier B	GAC 2	12 x 40	coconut	0.37	0.12	0.19	0.68
	GAC 3	12 x 40	coal	0.30	0.34	0.40	1.04
Supplier C	GAC 4	8 x 30	coal	0.30	0.19	0.26	0.75
	GAC 5	8 x 40	coal	0.28	0.15	0.78	1.21
Supplier D	GAC 6	8 x 30	coal	0.32	0.21	0.25	0.78
	GAC 7	8 x 30	coal	0.47	0.13	0.25	0.85

\* pore volume in cm<sup>3</sup>/g

### 6.2.3 Column trials

The rig comprised four 100 mm diameter polycarbonate columns mounted on a tubular steel frame, all associated pipework being attached to the frame via a GRP plate. Each column was filled with 1 L of GAC sample, retained by a fine mesh screen at the column base. Secondary effluent was pumped via a peristaltic pump to each column at a rate of 66 mL/min to achieve an EBCT of 15 mins (based on typical GAC design values (Eddy et al., 2002)). Each column was part filled with de-ionised water prior to slowly pouring in the GAC. The GAC was then left for a minimum of 24 h before operation to allow for de-aeration; subsequent introduction of air into the column through accidental draining was avoided at all times. Each column was fitted with an overflow to maintain a constant head. Samples were taken daily at the column inlet and outlet. The test was ceased once the reduction in organics was less than 50%.

### 6.2.4 Analytical methods

The extracted samples were analysed on site for turbidity, TOC, UV<sub>254nm</sub> and UV<sub>400nm</sub>, the latter relating to colour. TOC was measured using a Hach Lange Astro TOC UV turbo analyser, UV<sub>254nm</sub> and UV<sub>400nm</sub> using a Thermo Scientific Genesys 10 Spectrophotometer and turbidity was measured using a Merck Turbiquant 1500 IR.

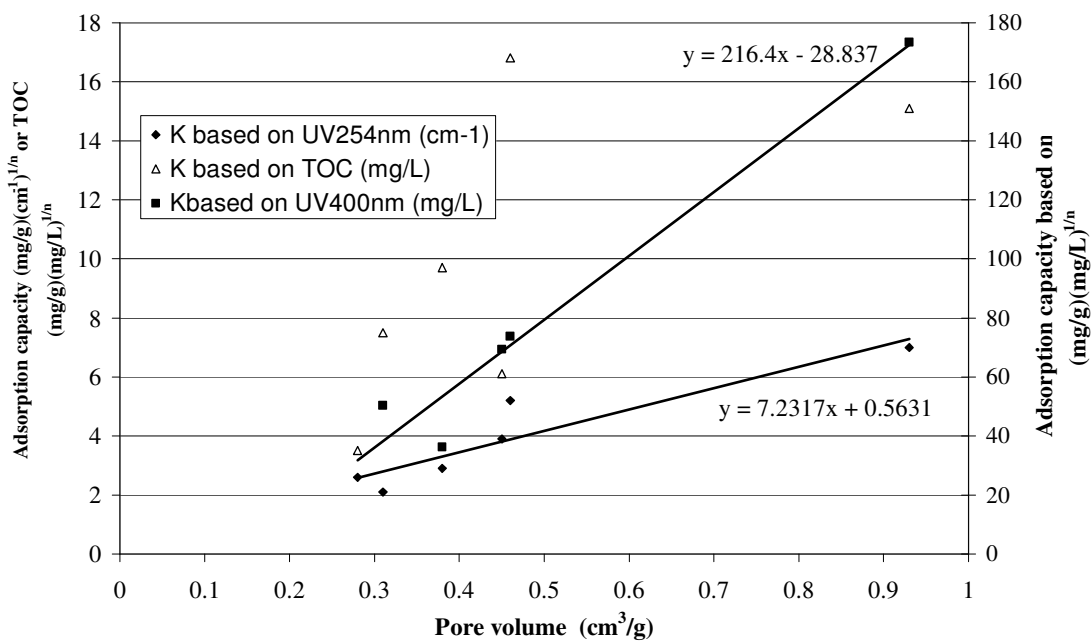
## 6.3 Results and discussion

### 6.3.1 Bench-scale tests

Table 6-4 shows the results of the isotherm tests at 20°C for the seven different GACs. Data were fitted to isotherms generated from the Freundlich model ( $q_e = K C_e^{1/n}$ ),  $q_e$  and  $C_e$  being the equilibrium surface and liquid concentrations respectively and  $K$  and  $1/n$  respectively relating ostensibly to the adsorbate capacity and the adsorption strength.

For the UV<sub>400nm</sub> (colour) adsorption isotherms of GACs 1 – 4 and the TOC isotherm for GAC 1, the data set showed two distinct zones: a strongly adsorbable zone represented by an almost vertical line and a moderately

adsorbable zone. The isotherm was fitted only to the data in the latter zone; extrapolating the isotherm to the high concentrations in the highly adsorbable zone is known to significantly underestimate adsorptive capacity (Frick and Sontheimer, 1983). In the case of GAC 1, all colour data were in the highly adsorbable zone: no isotherm could be fitted to these data, and the material had a lower capacity for colour compared to the other GACs.  $R^2$  values for correlations fitted to data in the moderately adsorbable zone ranged from 0.96 to 0.99, confirming the good fit of data to the Freundlich isotherm.



**Figure 6-1 Correlation between pore volume and adsorption capacity for each GAC tested.**

According to the adsorption data for all three water quality determinants (Table 6-4), there are wide differences in capacity according to the determinant used. From the GAC media tested the adsorption capacity  $K$  varied with base material, with the values for coal-based materials exceeding those based on coconut. Media 4, 5 and 6 provided the highest adsorption capacity independent of the determinant used. Adsorption capacity increased approximately with available macropore and mesopore volume with strong



correlation when organic removal was measured by UV<sub>400nm</sub> ( $R^2 \sim 0.96$ , Figure 6-1). However, the correlation was poorer for the UV<sub>254nm</sub> data ( $R^2 \sim 0.86$ ) and very poor for TOC ( $R^2 < 0.5$ ). This suggests that the adsorption capacity for non-aromatic and non-colour portion of the organic matter is not just related to pore size but some other media characteristic, such as surface chemistry. Moreover, the correlations do not pass through zero suggesting that some adsorption takes place in the micropores, as hypothesised by Newcombe (1999) The main exception to these correlations was GAC 3, whereby the adsorption capacity was 0.3-0.5 that expected from the available pore volume correlations. These finding are in partial agreement with Bjelopavlic et al (1999), who reported good correlation with the combined secondary micropore and mesopore volumes based on UV<sub>254nm</sub>, and Newcombe et al (1999) for correlations between DOC removed and mesopore volume. Differences in behaviour arise from the relationship between the organic matter molecular weight range and that of the pore size and volume.

**Table 6-4 Isotherm parameters for organic removal**

	TOC (mg/L)		UV <sub>254nm</sub> (cm <sup>-1</sup> )		UV <sub>400nm</sub> (mg/L)	
	K	1/n	K	1/n	K	1/n
GAC 1	3.5	0.85	2.6	0.72	nm	nm
GAC 2	7.5	0.63	2.1	0.49	50.4	0.11
GAC 3	10.5	0.48	3.1	0.54	45.2	0.36
GAC 4	6.1	0.96	3.9	0.47	69.4	0.47
GAC 5	15.1	0.60	7.0	0.57	173.4	0.24
GAC 6	16.8	0.64	5.2	0.57	73.8	0.49
GAC 7	9.7	0.63	2.9	0.49	36.3	0.58

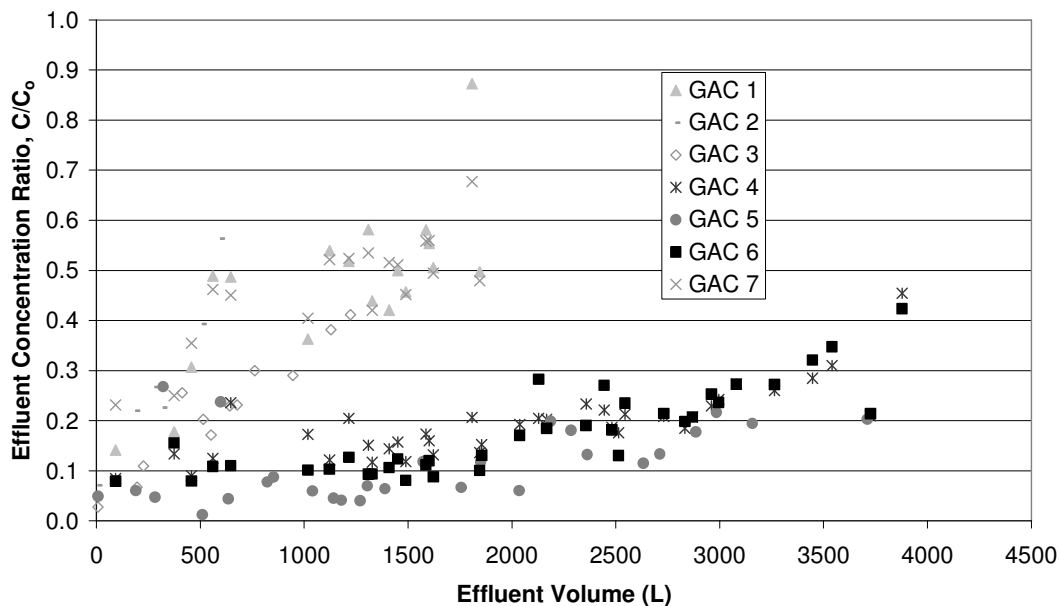
### 6.3.2 Column trials

Breakthrough curves of normalised effluent concentration ( $C/C_0$ ) against effluent volume for the media sample allow comparison of capacities, where the area above the curve represents the mass of adsorbate retained by the media column. UV<sub>254nm</sub> breakthrough data (Figure 6-2) were similar to those of TOC, with a residual concentration of 0-20% of the feed arising in the effluent at  $t = 0$  for all media. This percentage of the aromatic organic matter is evidently not adsorbable. However, the breakthrough curves for colour-forming organics

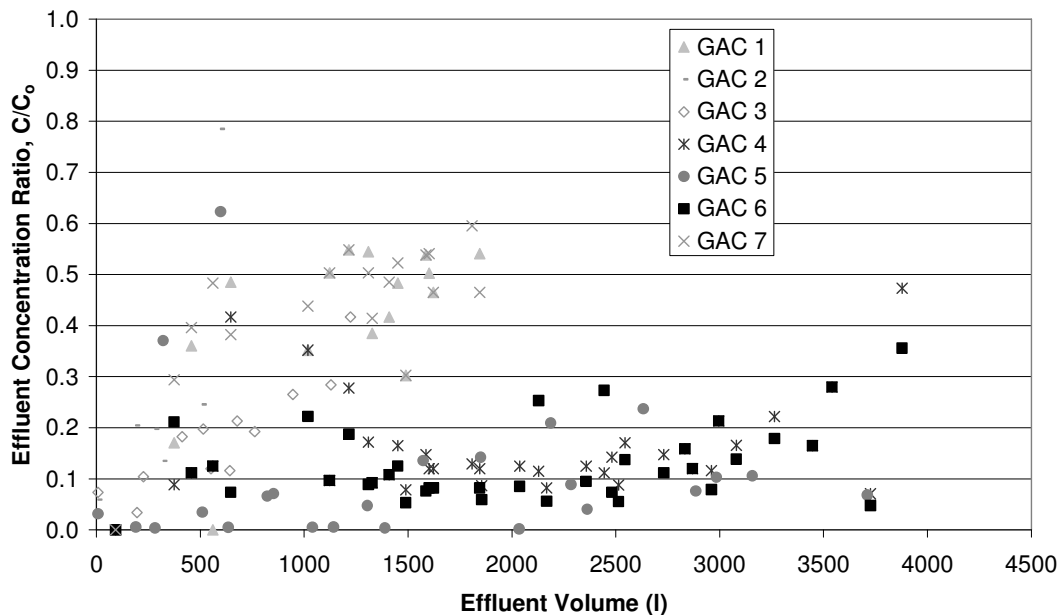
(UV<sub>400nm</sub>, Figure 6-3), suggest that these compounds are readily adsorbed with an outlet concentration close to zero being sustained.

Those GACs demonstrating the highest adsorption capacities at bench scale (4, 5 and 6) also providing superior organic removal during the column trials – 90% organic removal as TOC mg/L) or UV<sub>254nm</sub> for >1500 bed volumes (BV) compared to <500 BV for the other materials tested. Organic removal as measured by UV<sub>400nm</sub> resulted in a greater total treated volume (2500 BV) for samples 4, 5 and 6.

Based on the GAC material characteristics (Table 6-3), the outcomes suggest that the superior performance of GACs 4, 5 and 6 could be due to their coarser mesh size. However, GAC 7 did not follow this trend, and the data also contradict the findings from a survey of 63 US GAC treatment studies (Bond and DiGiano, 2004). This study of bituminous GAC of two different grain sizes (12 x 40 and 8 x 30) revealed that the finer grade (12 x 40) could treat 60% more BVs.



**Figure 6-2 Adsorption column breakthrough curve for EBCT = 15 mins (based on UV<sub>254nm</sub> removal)**

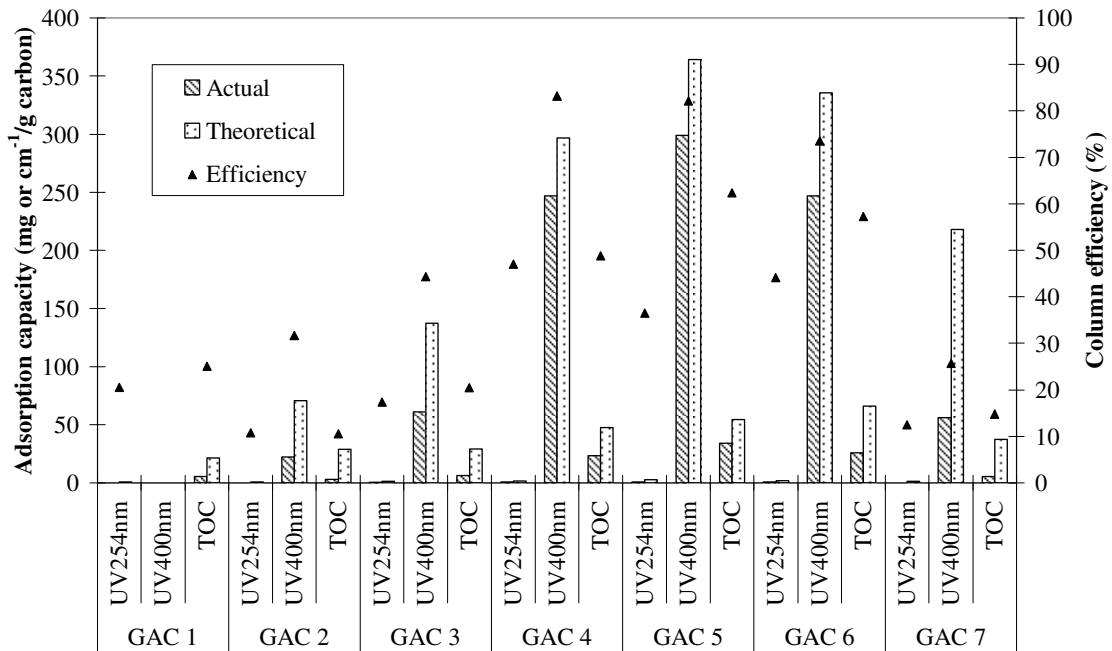


**Figure 6-3 Adsorption column breakthrough curve for EBCT = 15 mins (based on UV<sub>400nm</sub> removal)**

All tested media were found to reduce the turbidity from an average of 9.8 NTU to <2 NTU, i.e. >80 % removal, comparable to the results of Chinu et al (2009) and Graese et al (1987) for GAC media columns operating at similar EBCT values. However, there was no significant difference in removal across the different media tested, despite materials 1-3 being finer grade which would thus be expected to produce a greater reduction in turbidity than the coarser grades of 4-7. All the media tested would thus significantly reduce the solids load on the downstream membrane filter.

Figure 6-4 shows that, as expected, the theoretical capacity of the carbon based on the bench scale tests was higher than that achieved by the GAC columns. This is partially due to differences in rate of adsorption between the ground GAC used in the bench scale trials and the larger-grained GAC material used for the column tests. Adsorption rate is controlled by a combination of film

and intraparticle diffusion. The film diffusion is dependent on bulk flow which is usually rapid for the ground GAC due to the constant agitation during the bench scale trials compared to a column. Also, the adsorbent particle size is important in determining the diffusion path length and therefore the time required for transport within the particle to available adsorption sites. Hence diffusion is more rapid for ground GAC (Edzwald, 2011)



**Figure 6-4 Comparison, of actual adsorption capacity achieved by the column (based on breakthrough data) and theoretical adsorption capacity (based on jar tests) in absolute terms and as a percentage (column efficiency), assuming 80% organic removal.**

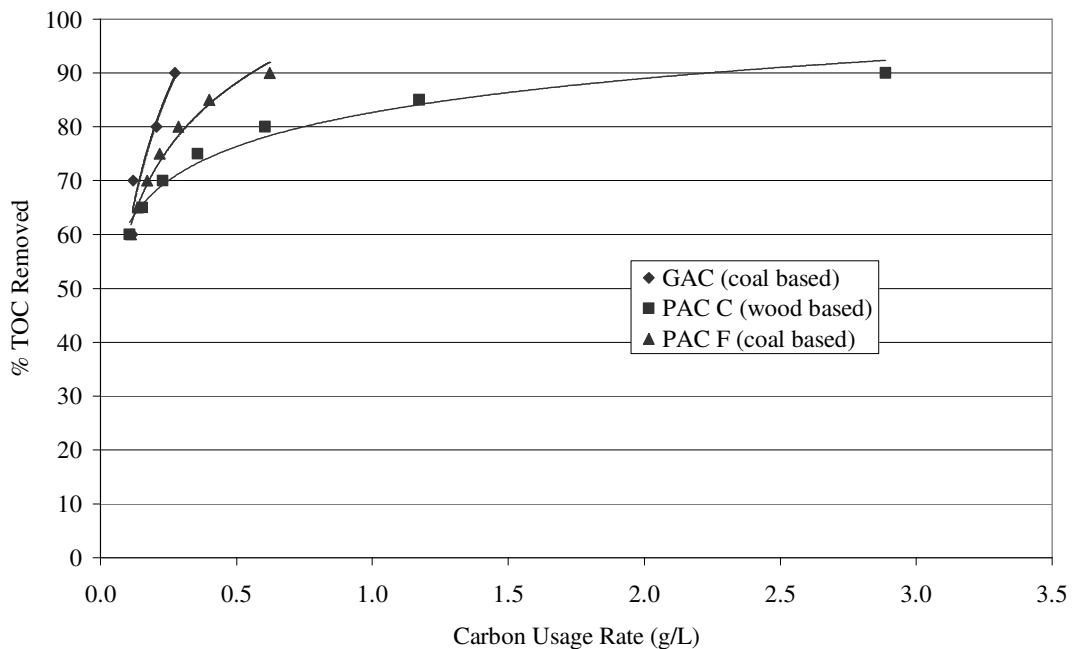
Figure 6-4 also shows that column efficiency (percentage of theoretical capacity achieved by the column) greatly varied from 11 to 83 % dependent on GAC and the method of measuring organic removal with those GACs with the highest adsorption capacity (4, 5 and 6) also having the highest efficiency especially based on UV<sub>400nm</sub>. Whilst wider than the range provided in text books (Eddy et al., 2002), Kalkan et al (2011) reported a removal efficiency 22% based on TOC from using Norit *PK1-3* peat-based GAC at a similar EBCT to the current work. This figure is also similar to that recorded for GACs 1, 2, 3 and 7, despite the

material Kalkan et al (2011) tested having similar range of pore volume as GAC 5; this demonstrates the difficulty in predicting performance from material characteristics. A possible explanation for the high removal efficiency based on  $UV_{400nm}$  is the underestimation of the theoretical capacity from extrapolation of the isotherm data to ambient influent  $UV_{400nm}$  concentrations. As previously mentioned (Section 3.1), the isotherms for GACs 1 - 4 demonstrated a highly adsorbable zone at high concentrations which were not included in the fitting of the isotherm. It is possible that GACs 5 – 7 would also demonstrate this highly adsorbable zone at the ambient influent concentration, but the practical limitations of jar testing at low AC concentrations make this difficult to verify. Therefore it is likely that the theoretical capacity was underestimated, so the column efficiency is artificially high.

### **6.3.3 Carbon usage rate (CUR)**

Previous work (Hatt et al., in press) assessed the addition of powdered activated carbon (PAC) to the immersed microfiltration (iMF) membranes. PAC addition was found to suppress irreversible fouling through reducing the organic load onto the membranes but had negligible impact on the reversible fouling rate. Attaining organic removal efficiencies above 60% demands significant PAC carbon usage (Figure 6-5), especially for PAC C, which is unlikely to be offset by any benefit in reduced chemical cleaning of the membrane. Increased organic removal from GAC demands comparatively less carbon usage. This concurs with the generally accepted practice that GAC is more economical than PAC for long-term usage at high organic loads (Edzwald, 2011). Higher capital costs associated with GAC are offset by simpler process control and manual handling (removal and exchange of the GAC on a 12 – 18 month basis), along with improved removal efficiencies resulting from equilibration at higher influent concentrations than the PAC. However, the turbidity load onto the GAC column would demand regular backwashing to limit pressure build-up, adding to operating expenditure (OPEX).

Whilst the current trials evaluated the GACs only at an EBCT of 15 minutes, a longer EBCT would be expected to lead to improved suspended solids removal (Graese et al., 1987) and more efficient use of the bed for adsorption due to the improved kinetics (Graese et al., 1987). The degree of improvement thus depends on the EBCT value and the adsorption kinetics. Whilst Schideman et al (2007) found the CUR for atrazine removal by a GAC fixed-bed to decrease markedly with increasing EBCT between 2 to 8 mins, the impact on increasing the EBCT further was negligible. Only minor reductions in CUR were reported from increasing the EBCT from 5.25 to 21 mins based on achieving 64% TOC removal in river water (Dvorak and Maher, 1999). On the other hand, improved CUR efficiencies were demonstrated by the latter authors from increasing the number of columns operating in parallel.



**Figure 6-5 Comparison of the carbon usage rates depending on the application of activated carbon (powdered or granular).**

## 6.4 Conclusions

The adsorption capacity and kinetics of seven different GACs were determined from bench scale adsorption studies using the Freundlich isotherm to fit the data. The adsorption capacity  $K$  measured as  $UV_{254nm}$ ,  $UV_{400nm}$  or TOC, varied with base material from 2.1-50.4 for coconut-based materials to 2.9-173.4 for coal-based ones. Media 4, 5 and 6 were shown to have the greatest adsorption capacity, attributed to their greater combined meso and micropore volumes.

Those GAC media (4, 5 and 6) demonstrating the greatest adsorption capacity at bench scale also proved to have superior adsorption capacity in media bed studies, providing 90% organic removal as TOC (mg/L) or  $UV_{254nm}$  for more than 1500 BV throughput compared to less than 500 BV for the other media tested. Bed capacities measured as  $UV_{400nm}$  were higher (>2500 BV) for samples 4, 5 and 6. All media tested gave similar results with regards to turbidity removal, reducing it by 80% to below 2 NTU. Whilst media 1-3 were of a finer grade than the other materials tested no greater turbidity reduction resulted.

Based on organic removal rates above 70%, the use of GAC media is calculated to provide a significantly lower (30 – 90 %) carbon usage rate (CUR) than that previously reported for the powdered form in protecting the downstream microfilter (MF). Further pilot plant trials are required to assess the benefit of GAC on the downstream processing based on reduced cleaning and improved water quality of the MF against the additional costs incurred from installing and operating the GAC column.

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## **CHAPTER 7: Membrane pretreatment for water reuse: a cost analysis**



## 7.1 Introduction

Membrane fouling by natural organic matter (NOM) remains a key constraint in the application of membrane filtration technology to water treatment, with much research generated. Early studies (Wiesner et al., 1989) revealed the colloidal fraction of natural organic matter to contribute most significantly to fouling in microfiltration (MF) and ultrafiltration (UF) membranes resulting in the need for frequent backwashing and chemical cleaning leading to high operating expenditure (OPEX) and reduced throughput. Fouling amelioration can be achieved through use of pretreatment which can alter the physical, chemical and/or biological properties of the feed water resulting in improved membrane performance both with regards to reduced downtime and cleaning requirements but also improved product water quality.

The most commonly used pretreatment is coagulation, which alters the chemical properties of the feed water to destabilise contaminants so that they aggregate to form larger particles which are rejected by the membrane rather than plug the membrane pores. If larger doses of coagulant are applied the resulting aggregates can be removed via settlement upstream of the membranes. Coagulation has been found to be particularly effective in removing aromatic NOM species with a high molecular weight (MW) and hydrophobicity (Edzwald and Van Benschoten, 1990), which some studies have found to be the main cause of membrane fouling. However, whilst some authors (2009, Citulski et al., 2008, Qin et al., 2004) reported coagulant dosing to reduce the feedwater colloidal content and fouling propensity, others (Karimi et al., 1999, Schäfer et al., 2001) have found the reverse. Nonetheless, fouling suppression via coagulation is not contingent on organic removal: very low doses of coagulant have been shown to be effective in suppressing fouling without providing organic removal (Hatt et al., 2011, Shon et al., 2005, Konieczny et al., 2009).

Adsorption using activated carbon (AC) provides an alternative MF/UF pretreatment, and can be used in the granular form as a media bed or dosed inline in powdered form. As well as reducing fouling in some cases (Best et al.,

1999, Zhang et al., 2011), AC may also improve NOM removal by MF/UF as well as micropollutants such as pesticides and taste and odour-forming compounds. These trace pollutants are of particular concern in indirect potable reuse.

Sanitation with chlorine can suppress the growth of micro-organisms and so reduce biological fouling, but at the risk of generating disinfection byproducts (DBPs). Ozonation may also be used to improve removal of turbidity (Chang et al., 2001) or colour (Park et al., 2010, Nguyen and Roddick, 2010) of a UF process, as well as improving permeability (Hashino et al., 2000, 2001), but it may also lead to DBP formation, namely bromate. Ozone partially oxidises the NOM into lower MW species and more polar species which are more biodegradable and therefore may actually exacerbate biofouling, rather than provide sanitation. Moreover, ozone is not compatible with most polymeric membranes.

Prefiltration can be used to reduce the concentration of those materials contributing to membrane cake layer formation and/or clogging, and reduce the number of micro-organisms which may cause bio-fouling. Pretreatment of secondary effluent using a slow sand filter has been shown to decrease the fouling rate by up to 60 times (Zheng et al., 2009), with similar results reported for granular media pretreatment (Bourgeois et al., 2001). However, the prefilter requires maintenance cleaning in the same way as a membrane filter, and this has associated cost implications.

A range of MF pretreatment processes have been evaluated based on the outcomes of the individual studies already reported (Chapters 1-5). This work aims to compare the findings for each of the pretreatment methods evaluated and identify the one(s) most effective for membrane fouling suppression, water quality improvement and OPEX reduction. The implications of pre-treatment on downstream processes is also considered.

## 7.2 Materials and methods

### 7.2.1 Pilot Plant

The 600 m<sup>3</sup>/d pilot plant has been described elsewhere (Raffin et al., 2011b). It receives secondary effluent (Table 7-1) from a conventional activated sludge-based municipal wastewater treatment works in north London, UK. It comprises a 500 µm-rated automatically backflushed pre-filter (Bollfilter model 6.18) upstream of the MF skid, which comprised 16 immersed microfiltration (MF) membrane modules (Siemens Memcor CMF-S 0.04 µm). MF permeate is fed to a reverse osmosis (RO) unit (Hydranautics ESPA-2) and/or a hydrogen peroxide-UV advanced oxidation process (AOP). Chloramine may be dosed at a number of points in the process, including prior to the pre-filter. The main operating parameters are summarised in Table 7-2.

**Table 7-1 Feed water quality parameters, Jan 2009 – Jan 2012**

Parameter	Mean	Standard deviation
Turbidity (NTU)	4.9	3.1 (63%)
TOC (mg/L)	7.4	2.5 (34%)
pH	6.9	0.3 (4%)
Temperature (°C)	17.5	3.1 (18%)
Alkalinity (mg/L CaCO <sub>3</sub> ) *	195.3	14.1 (7%)
TSS (mg/L) *	8.0	5.6 (70%)

All from continuous online monitoring other than \*based on periodic spot sampling

### 7.2.2 Pretreatment

A number of pretreatment methods have been evaluated in the course of this study, with specific variables and recorded impacts being:

- Impact of prefilter rating on operability and reducing the rate of downstream MF fouling (Chapter 2)
- Impact of chloramine dosing on water quality only (Chapter 3)
- Impact of in-line coagulant dosing on reducing the rate of downstream MF fouling and permeate water quality (Chapter 4)

- Impact of in-line PAC dosing on reducing the rate of downstream MF fouling and permeate water quality (Chapter 5)
- Impact of in-line fixed GAC media bed on reducing the rate of downstream MF fouling and permeate water quality (Chapter 6)

**Table 7-2 Pilot plant operating parameters**

Process	Operating parameters	References
Pre-filter	Mesh size: 500 µm Backwash flow: 8.5 m <sup>3</sup> /h for 20 s	Hatt et al, Chapter 1
Chloramine Microfiltration (MF)	Chloramine dose 1 ppm Flux: 40 LMH Backwash interval: 30 min using air and water. Backwash downtime of 300 s CIP: 600 ppm as Cl of sodium hypochlorite at 35 °C	(Raffin et al., 2011a, Raffin et al., 2011b)
Reverse osmosis (RO)	Flux: 19 LMH Recovery: 75% Sulphuric acid to reduce pH to 6.75 Antiscalant dose: 2 ppm CIP: Hydrochloric acid at pH 2.5 and 35 °C	(Raffin et al., 2011b)
Advanced oxidation process (AOP)	After MF Power: 100% Hydrogen peroxide dose: 16 mg/L After RO: Power : 60% Hydrogen peroxide dose: 3 mg/L	(James et al., 2011)
Post-treatment	Sodium hydroxide to increase pH to 7-8 (RO stream only)	

### 7.2.3 Fouling assessment

Membrane fouling is manifested as a change in transmembrane pressure (TMP) with time at constant flux. The reversible fouling rate is considered to be that which can be physically removed, in this case by periodic backwashing with air and water for 5 mins every 30 mins. The reversible fouling rate is thus the rate of TMP increase between backwashes (the filtration cycle), and the reversible fouling factor is the rate of change of reversible fouling rate with mean feedwater turbidity during the filtration cycle. Irreversible fouling is ascribed to fouling which is not removed by backwashing and requires chemical



cleaning to restore permeability. It is manifested as the rate of change of TMP recorded immediately after backwashing.

#### **7.2.4 Water quality assessment**

The two key parameters of feed water quality which affect MF fouling rate and so its operation and maintenance (O&M) requirements are the turbidity and the organic carbon concentration (reflected as total organic carbon (TOC),  $UV_{254nm}$  and  $UV_{400nm}$ ). Pretreatment improves MF performance either by reducing the foulant load onto the MF (in the case of the prefilter/GAC) or protecting it (coagulation or PAC), and therefore also improving the MF permeate quality. The effectiveness of pretreatment was thus assessed by monitoring the organic concentration and turbidity before and after both the pretreatment and MF stages, as well as monitoring TMP rates.

The key deleterious impact of chloramine dosing is on permeate water quality, specifically formation of the disinfection byproduct (DBP) N-nitrosodimethylamine (NDMA). NDMA, a known carcinogen, can be generated from chloramine addition to secondary effluent (Najm and Trussell, 2001, Sedlak et al., 2005). Work by Raffin et al (2011b) found that doses up to 1 mg Cl/L had no impact on fouling mitigation. Therefore, before chloramine doses > 1 mg Cl/L were evaluated for the purposes of reducing biofouling, the effect on NDMA formation needed to be assessed first. As well as monitoring NDMA concentration in the secondary effluent following chloramine dosing, levels of ammonia and free chlorine were also monitored.

#### **7.2.5 Analytical methods**

The pilot plant was fully automated and data recorded on a supervisory control and data acquisition system (SCADA). Online instrumentation included:

Siemens Magflow 6000 flowmeters on the prefilter (feed, discharge and backflush lines) and the MF (feed and permeate lines);

Hach Lange turbidity meter on the prefilter (feed and discharge) and the MF (feed and permeate);

Hach Lange pH, TOC, ammonia, and DO monitoring on the feed to the prefilter;  
chlorine meter on the prefilter discharge;

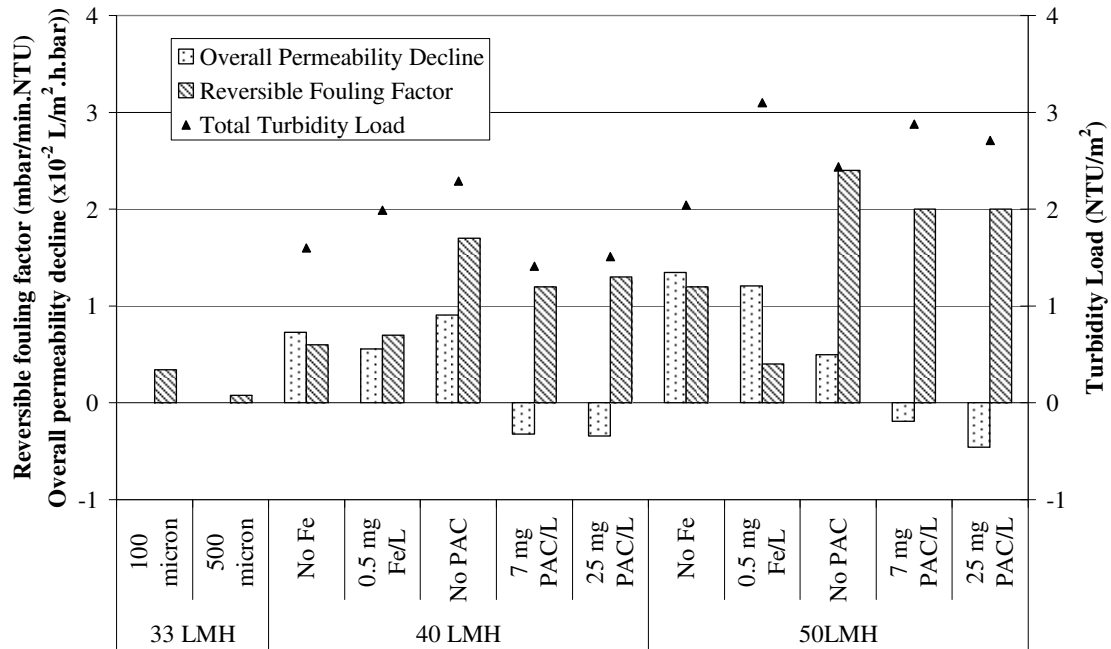
ABB pH and temperature monitoring on the MF permeate.

Grab samples taken before and after each pretreatment process evaluated were analysed on site for turbidity, TOC, UV<sub>254nm</sub> and UV<sub>400nm</sub>. TOC was measured using a Hach Lange Astro TOC UV turbo analyser, UV<sub>254nm</sub> and UV<sub>400nm</sub> using a Thermo Scientific Genesys 10 Spectrophotometer and turbidity using a Merck Turbiquant 1500 IR. Samples were also periodically taken and analysed by Thames Water Laboratory for total suspended solids (TSS) and alkalinity measurement according to standard methods (Eaton et al., 2005).

## **7.3 Results and discussion**

### **7.3.1 Impact on microfiltration fouling rate**

Figure 7-1 shows the effect of different pretreatments on the reversible fouling factor. The effect of mesh size used in the prefilter on the reversible fouling factor was only evaluated at 33 LMH whilst all other trials were at 40 or 50 LMH. However, Figure 7-1 clearly shows that reducing the mesh size from 500 to 100  $\mu\text{m}$  results in a four fold increase in the reversible fouling factor.



**Figure 7-1 Impact of different pretreatment methods on membrane fouling.**

At both 40 and 50 LMH, there is step change in the reversible fouling factor when comparing those results performed at 0 and 0.5 mg Fe/L ferric sulphate with those at 0, 7 and 25 mg/L PAC. This step change could be attributed to the difference in temperature of the secondary effluent used during these trials, 20 and 12°C respectively. The data was normalised to 20 °C for viscosity correction, though this is known to underestimate temperature impacts since it ignores those on the membrane material (Amin et al., 2010) and particle back transport (Jiang et al., 2005). Application of 0.5 mg Fe/L ferric sulphate had a negligible effect on the reversible fouling factor at 40 LMH, whereas the use of PAC reduced the fouling by 17-35 %. However, this reduction is insufficient to enable the filtration cycle to be significantly extended to, say, 45 mins since this would require the fouling rate to be below 12 mbar/min which can only be achieved if the turbidity is <8 NTU. At 50 LMH, a ferric dose of 0.5 mg Fe/L led to a significant reduction in the reversible fouling factor enabling the plant to run for more than 14 days between chemical cleans, twice as long as could be achieved without ferric dosing. This would imply that the use of a small dose of

ferric could enable a 25 % higher flux to be maintained by the microfiltration plant which would result in a 20 % smaller membrane plant.

The impact of pretreatment on irreversible fouling, which demands chemical cleaning for its removal, is manifested as a reduction in permeability decline (Figure 7-1). At both 40 and 50 LMH, dosing ferric reduced the decline in permeability whilst dosing with PAC reversed the decline, implying a significant reduction in chemical cleaning frequency. However, long-term use of PAC could result in increased attrition of the membrane fibres, although there was no evidence of this from the membrane integrity tests over the course of the 4-month trial.

Although GAC pretreatment was not evaluated at pilot plant scale, the product water from the columns was consistently <2 NTU (Table 7-3). From the correlation of reversible fouling rate change with turbidity produced for pilot scale operation, a turbidity of  $\leq 2$  NTU would be expected to reduce the reversible fouling rate to below 2 mbar/min, implying a filtration cycle time above 1 h. This would increase water recovery (by >1 % to 99 %) and, more importantly, enable the MF to run sustainably at 50 LMH or more, thereby reducing CAPEX.

### **7.3.2 Water quality**

Neither reduction of the prefilter mesh size nor dosing with 0.5 mg Fe/L ferric sulphate impacted on water quality (Table 7-3). However, pretreatment using AC both in powdered and granular forms significantly reduced organic levels in accordance with PAC dose or GAC column regeneration frequency, benefitting overall water reuse process efficacy for a water reuse schemes incorporating an advanced oxidation process (AOP). In particular, the AOP hydrogen peroxide and UV dose relate directly to the percentage UV transmittance (UVT) of the water (James et al., 2011). Application of either PAC or GAC increased UVT from 69 to 92% based on  $UV_{254nm}$  ( $cm^{-1}$ ) depending on PAC dose or GAC regeneration frequency, approaching the rejection achieved by the RO (99 %). This implies pretreatment of an MF-AOP with AC would greatly lower the OPEX of the AOP (as determined by the UV and peroxide doses) and may ultimately

obviate the RO step entirely if the water quality attained is sufficient for the reuse application intended. It is also the case that GAC pretreatment was the only method impacting on turbidity, considered to be the main cause of membrane fouling (Li et al., 2010), reducing it to consistently below 2 NTU.

Trials performed to assess the impact of chloramine dose between 2 and 5 mg Cl/L indicate that (Table 7-4), at both concentrations, NDMA levels significantly exceeding the DWI guideline value of 10 ng/L arise at higher temperatures (i.e. during summer months) and a pH 7 at the lower dose, and under all conditions at the higher dose. The use of elevated chloramine levels for MF biofouling mitigation is thus problematic if the end use is indirect potable reuse without further dilution. Therefore trials to assess the effect of elevated chloramine doses on fouling amelioration were not performed.

**Table 7-3 Impact of different treatments on water quality**

	pre-MF	post-MF				
	Turbidity (NTU)	Turbidity (NTU)	TOC (mg/L)	UV <sub>254nm</sub> (cm <sup>-1</sup> )	UVT (%)	UV <sub>400nm</sub> (mg/L)
Prefilter 500 µm mesh size	5.0	<0.2	6.8	0.158	69	20.0
Prefilter 100 µm mesh size	5.0	<0.2	6.8	0.158	69	20.0
Ferric Addition	5.0	<0.2	6.8	0.158	69	20.0
PAC Addition 5 mg/L	5.0	<0.2	6.2	0.144	72	9.4
PAC Addition 25 mg/L	5.0	<0.2	5.2	0.114	77	4.0
PAC Addition 50 mg/L	5.0	<0.2	5.2	0.097	80	4.0
GAC to provide 30 % TOC removal	<2	<0.2	5.2	0.086	82	8.0
GAC to provide 50 % TOC removal	<2	<0.2	3.7	0.062	87	5.2
GAC to provide 60 % TOC removal	<2	<0.2	3.0	0.052	89	4.0
GAC to provide 75 % TOC removal	<2	<0.2	1.8	0.036	92	2.0

**Table 7-4 Impact of operating conditions on NDMA formation (ng/L)**

Chloramine dose (mg Cl/L)	pH 6 / 10 °C	pH 7 / 10 °C	pH 6 / 25 °C	pH 7 / 25 °C
2	3	4	3	141
5	23	33	43	359

### 7.3.3 Cost analysis

Simplistic cost analysis has been carried out based on current prices for major OPEX items as shown in Table 7-5 such as membrane replacement (based on replacing the MF membranes every 7 years and the RO every 5 years), chemical costs (pretreatment chemicals such as ferric sulphate, PAC and GAC as well as those for chemically cleaning the MF (sodium hypochlorite) and hydrogen peroxide for AOP), electricity costs for the RO feed pump and UV dose for the AOP (both based on pilot plant experiences and a current commercial electricity price of (10 p/kWh)).

**Table 7-5 Current prices for major OPEX prices used on the pilot plant**

Reagent	Per kg	Reagent	Per te	Item	Per/m <sup>2</sup>
PAC	£1.50	Ferric sulphate 13.5 %	£107	MF module	£18.60
GAC	£1.40	Hydrogen peroxide 35 %	£666	4" RO membrane	£20.25
Antiscalant	£2.60	Sodium hypochlorite 14/15 %	£299	8" RO membrane	£11.32
Hydrochloric acid	£7.60	Sulphuric acid 30 %	£118		
		Sodium hydroxide	£126		

Results show that ferric dosing can enable sustained operation at a 25 % higher flux. This results in a 20 % reduction in required membrane area, and a commensurate reduction in capital expenditure (CAPEX) through membrane and tankage costs and reduced footprint, leading to a cost saving of approx. 0.09 p/m<sup>3</sup> (Table 7-6 and Chapter 3). Further cost savings could be made by only dosing when required. For example if ferric was only dosed at feedwater turbidities above 5 NTU, then the cost of dosing would decrease by 67 % increasing OPEX savings to 0.12 p/m<sup>3</sup>.

Table 7-6 shows that the AC cost is significant when compared with the potential cost savings through reduced chemical cleaning of the MF, and reduced hydrogen peroxide and UV dose for the AOP. Pianta et al (2000, 1998) also found that PAC as a pretreatment of MF/UF provided significantly increased O&M costs due not only to the cost of PAC but also increased energy costs from running the membranes in cross flow mode rather than dead-end to

ensure the plant could handle high turbidity events. Dosing PAC at 5 mg/L could provide a more cost effective means of controlling fouling if, as with pre-coagulation, it is applied only during high turbidity events (>5 NTU) thereby reducing OPEX by 67 %. However, this assumes that the permeate quality improvements are sustained during low turbidity periods to enable reductions in AOP OPEX costs.

As already stated, the application of AC as a pre-treatment for MF for wastewater reuse may become cost effective if obviating the downstream RO step for both an MF-RO and an MF-RO-AOP process, where the AOP may be demanded to remove residual problem organic materials (Drewes and Khan, 2011). As can be seen from Table 7-6, the cost savings accrued by obviating the RO imply that the use of PAC up to a dose of 50 mg/L becomes cost effective, although the cost of the increase in dose from 25 to 50 mg/L is unlikely to be justified by the small improvement in water quality attained. However the OPEX cost of running a GAC column appears to be greater than that of an RO skid, contrary to the findings of Schimmoller et al. (2011). Schimmoller et al (2011) found RO OPEX to be more than 14 times greater than that for GAC based on 50 % TOC removal. However, this is based on an influent TOC value of 4.6 mg/L which is 40 % less than the influent TOC in this work, therefore the number of bed volumes which they could process before regeneration is required will be greater. However, Helmy et al (2009) found that once regeneration frequency is increased to four times per year GAC yields a higher OPEX than for RO. This concurs with the findings of Wiesner et al. (1987) who found that GAC was cost effective for TOC removals up to 75% but only for treating waters with low TOC (2 mg/L). Moreover, the logistics GAC regeneration, which normally takes 3-4 weeks in the UK, would demand substantial redundancy to maintain operation. Thus, a high TOC level in the feed would imply MF-RO to be more cost effective than GAC-MF when low organic content in the produced water is important.

**Table 7-6 Cost savings (p/m<sup>3</sup>) associated with each pretreatments evaluated**

Microfiltration Pretreatment Evaluated	Pre-treatment	MF		RO membranes, chemicals & pumping	AOP		Net Saving
		CIP Chemicals + Energy	Reduced no. of membranes		Reduced H <sub>2</sub> O <sub>2</sub> Dose	Reduced UV dose	
0.5 mg/L Ferric Sulphate	-0.05	0.00	0.14	0.00	0.00	0.00	0.09
0.5 mg/L Ferric on demand	-0.02	0.00	0.14	0.00	0.00	0.00	0.12
5 mg/L PAC	-0.75	0.20	0.00	0.00	0.38	0.08	-0.09
5 mg/L PAC on demand	-0.25	0.20	0.00	0.00	0.26	0.05	0.26
25 mg/L PAC	-3.75	0.20	0.00	7.29	0.70	0.14	4.59
50 mg/L PAC	-7.50	0.20	0.00	7.29	0.90	0.18	1.07
GAC* based on							
30 % TOC removal (6 regen./y)	-9.57	0.20	0.14	7.29	1.02	0.21	-0.71
50 % TOC removal (8 regen./y)	-12.48	0.20	0.14	7.29	1.34	0.27	-3.24
60 % TOC removal (9 regen./y)	-14.35	0.20	0.14	7.29	1.47	0.30	-4.95
75 % TOC removal (12 regen./y)	-19.13	0.20	0.14	7.29	1.66	0.34	-9.50

\*Regeneration frequency estimated based on an empty bed contact time of 15 mins.

## 7.4 Conclusions

Evaluation of the pretreatment technologies employed for indirect potable water reuse have revealed the following practical facets:

1. Reduction of the prefilter mesh size from 500 to 100 µm resulted in a four-fold increase in MF fouling and no improvement in water quality. Thus, somewhat counter-intuitively, the larger mesh size is more effective than the smaller one.
2. The chloramine dose, applied for biofilm growth control, should not be allowed to increase to 2 mg/L during the summer months if NDMA levels directed by DWI guidelines are to be adhered to.
3. The addition of 0.5 mg Fe/L of ferric sulphate enables MF operation at a 25 % higher flux of (50 LMH cf. 40 LMH), reducing the membrane area requirement by 20 % and enabling a commensurate cost saving of 0.09 p/m<sup>3</sup>. This cost benefit is further increased if dosing is employed only during high turbidity events which, if a threshold of 5 NTU is chosen, would reduce the ferric consumption by 67 % and provide a cost saving of 0.12 p/m<sup>3</sup> overall.



4. The cost of using activated carbon (powdered or granular) as a pretreatment is high compared to the potential savings obtained in reduced chemical costs for the MF and AOP and lower power consumption of the AOP through reduced UV dose. Low doses of PAC (5 mg/L) may be cost effective if only applied during high turbidity periods, but this is dependent on the MF permeate water quality being maintained by periodic PAC dosing to enable the cost savings to be made on the AOP.
5. High doses of PAC (25-50 mg/L) could be cost effective if the improvement in water quality is sufficient to obviate the RO process downstream of the MF, on the basis of the target water quality with respect to the organic content being attained.
6. At the relatively high TOC concentrations associated with secondary effluent, the GAC media would require frequent regeneration to maintain removal of TOC, even by only 30%, whereas RO could produce a much higher water quality at lower OPEX. GAC is thus an unsuitable pretreatment method for this application.

## 7.5 References

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## **CHAPTER 8: Further Work**





This work has concentrated on those pretreatment methods which would not only reduce membrane fouling but which also may improve the water quality of the MF permeate. Other options which may prove beneficial at reducing the turbidity but without necessarily reducing the organic content are sand filters or alternative prefilters such as disk filters which use finer screens but have improved backwashing which can handle any biofouling. However unlike the technologies evaluated in this thesis these alternatives require significant CAPEX and hence have not been trialed so far. If this project was to be continued then an alternative prefilter could be assessed which should include a more thorough backwash facility to avoid the build up of biofouling. This would enable trials with finer screens to be evaluated with respect to reduction of turbidity and membrane fouling.

The OPEX analysis showed that it is unlikely that GAC would be cost effective as a pretreatment. However, there were a number of operational problems encountered during these trials. These included an infrequent feed supply to the columns due to low flows through the wastewater treatment plant which provided the feed, and no backwash facility on the columns such that solids build-up had to be removed manually. The column had a very low down flowrate (<1m/h) due to its dimensions although the empty bed contact time was set to a typical industry standard value of 15 mins. These factors may have adversely affected the results. Also, no consideration was given to using the columns in series or parallel which can reduce regeneration frequency. Rectification of these issues and repeating the trials with the one or two best performing GACs may lead to improvement in the number of bed volumes handled before regeneration is required, and improve the cost effectiveness of this as a pretreatment.

Assessment of the use of GAC at pilot scale as pretreatment to the MF would confirm the benefits of the consistently low turbidity effluent from the GAC in reducing fouling of the MF, and enable trials at flux rates in excess of 40 LMH to be evaluated. The cost analysis in this thesis assumed that using the GAC as a pretreatment would only result in a modest flux increase to 50 LMH. However,

this may be an underestimate. This pilot trial would also enable the cost saving on the AOP in terms of reduced hydrogen peroxide dose, UV dose and reduced cleaning requirements to be confirmed.

Due to the restrictions in the number of samples that could be handled by either laboratory and the associated costs involved in NDMA analysis the testing was carried out in small batches and each test only carried out twice. The fact that a number of different water samples were used during each test added an extra degree of variability that was not accounted for in the full factorial analysis. Therefore to fully validate the findings it would be beneficial to repeat the tests using only one water sample for the full range of test conditions as well as evaluating further residence times and temperatures.

Assessment of the benefits of recycling the powdered activated carbon (PAC) after the backwash would broaden the practical scope of the study. Schemes which commonly use PAC with membranes for taste and odour control recirculate the PAC from the membrane tank to a fixed bed reactor. This increases the residence time of the PAC enabling more of the adsorption capacity of the PAC to be realised before it is wasted and thereby reducing the dose of PAC to be applied.



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## **APPENDIX**

The basis of this thesis was to evaluate the effect of various pretreatment methods on fouling amelioration, assessed by the effect on reversible and irreversible fouling rates. This Appendix details the methods used for calculating these metrics.

## 1. Calculation of the Reversible Fouling Rate

The pilot plant including the membrane microfiltration unit was fully automated and all online monitoring was recorded at one minute intervals on SCADA. This monitoring included the transmembrane pressure (TMP) across the membranes, temperature and turbidity of the secondary effluent entering the pilot plant, membrane feed flowrate, permeate flowrate and permeate turbidity. Figure 1 shows how under constant flux conditions, the TMP (normalized to 20°C) increases linearly during each filtration cycle. Backwashing removes the foulants which have built up on the membrane surface during filtration, reducing the TMP towards its initial value, before starting to increase during the course of the next filtration cycle. This rate of change in TMP during a filtration cycle is known as the reversible fouling rate.

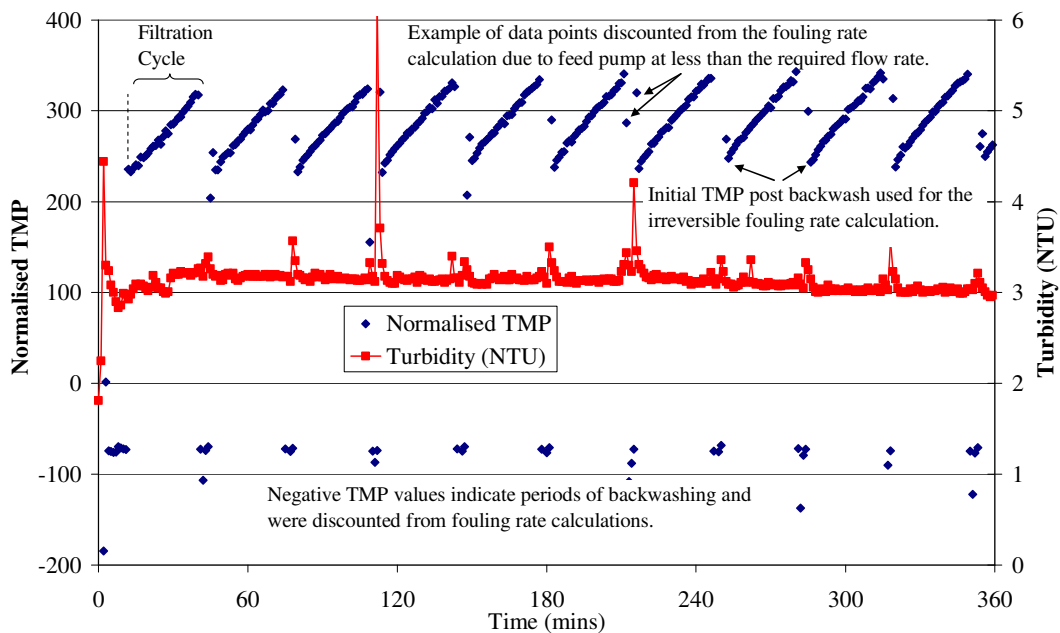
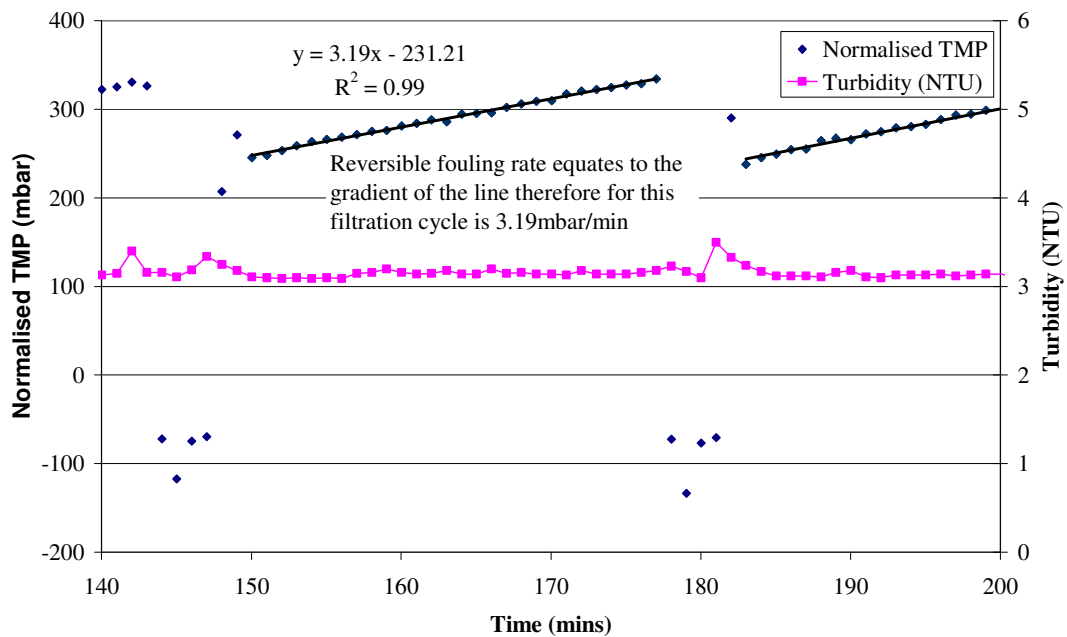


Figure 1 – Example of the variation in TMP during normal operation.

Each pretreatment was tested for a minimum period of 6 hours. The normalized TMP values for each filtration cycle during the test period were plotted in Excel against time and Excel's linear regression function used to calculate the gradient of the resulting fit which equates to the reversible fouling rate (Figure 2). The TMP readings during backwashing and at the very start and end of the filtration cycle when the feed pump was not producing the required flow were discounted from the reversible fouling rate calculation. The average turbidity of the secondary effluent feeding the microfiltration unit was also calculated for each filtration cycle. The reversible fouling rate for each filtration cycle was then plotted against the corresponding average turbidity for that filtration cycle. The gradient of the resulting linear plot enabled different pretreatments to be compared.

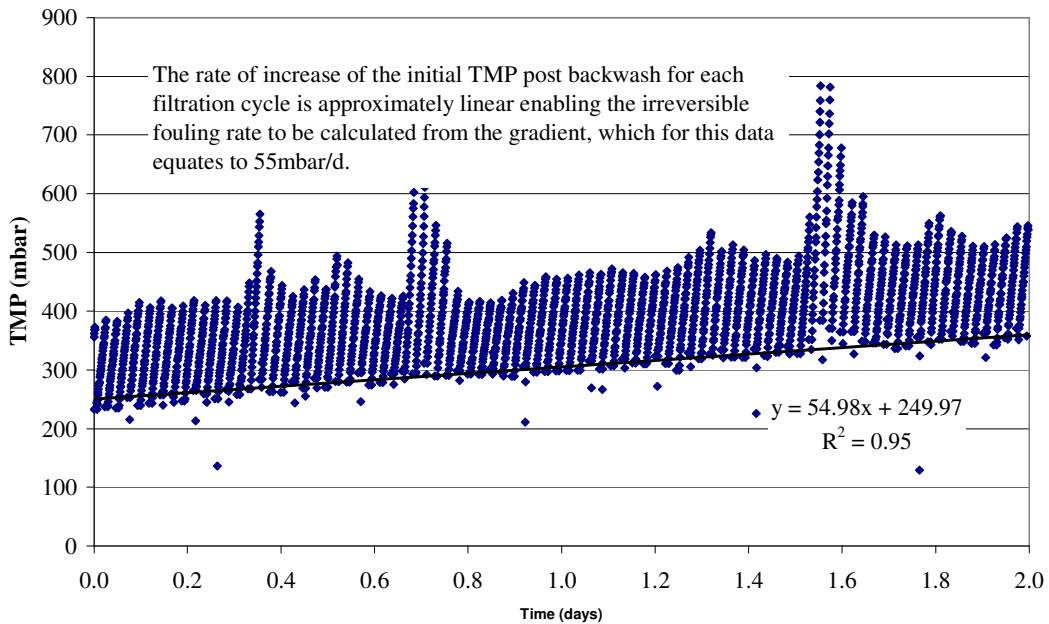


**Figure 2 – Example of the calculation of the reversible fouling rate for one filtration cycle using microfiltration data from the pre-coagulation trials (0.5 mg/L aluminium sulphate at 40 LMH).**



## 2. Calculation of the irreversible fouling rate

As mentioned above, backwashing restores the TMP. However, backwashing is not always sufficient to restore the TMP fully to its initial value due to a slow build-up of foulants which cannot be removed by backwashing alone. Figure 3 demonstrates this gradual increase in post backwash TMP, which appears to be linear over the time scale used for the pre-treatment trials. This rate of increase in the post backwash TMP is known as the irreversible fouling rate. As with the reversible fouling rate, the post backwash TMP was plotted against time within Excel and the linear regression function used to calculate the gradient of the resulting fit which equates to the irreversible fouling rate (Figure 3).



**Figure 3 – Example of the calculation of the irreversible fouling rate based on microfiltration data at 50 LMH with no coagulant or PAC dosing**

## 3. Calculation of permeability

Permeability is the measure of ease of flow through the membrane and is represented by the ratio of permeate flux (LMH) to TMP (bar). As flux is

constant, an increase in TMP will result in a reduction in permeability. The permeability at the start and end of each test period was calculated and the difference normalized with respect to time to enable comparisons to be made between pretreatments regardless of test period length. Permeability is inversely proportional to the resistance which includes the resistance due to the membrane and the fouling layer. As the membrane resistance will be constant (assuming constant temperature through the test period) and the rate of fouling was found to be linear, it was assumed that the change in permeability with time would be linear.