Hybrid Membrane Processes for Water Treatment
Hybrid membrane processes for water treatment

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CSIRO Molecular Science

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Executive Summary

Both microfiltration (MF) and ultrafiltration (UF) membrane processes have been used for potable water treatment, where they have been found to be particularly suitable for the removal of finely divided suspended solids, especially bacteria, algae and protozoa such as Giardia and Cryptosporidium. They have been less successful in cost terms for the removal of dissolved contaminants such as colour and chemical pollutants. The application of ultra-fine membrane structures (e.g. nanofiltration - NF and reverse osmosis - R/O) for the removal of soluble contaminants from drinking water suffers from high operating costs associated with high pressure drops and irreversible membrane fouling. There is significant potential for modification of water treatment systems to achieve the relatively low operating costs of microfiltration membrane systems while simultaneously achieving soluble contaminant removal.

A three year CRC for Water Quality and Treatment (CRCWQ&T) project was initiated to focus on the role of coagulation and adsorption processes in combination with microfiltration membrane processes. It was anticipated that by studying such process combinations, the removal of natural organic matter (NOM) on conventional microfiltration membranes could be achieved with minimal fouling of the membrane surface. The potential advantage of this combination of processes would be the development of low operating cost membrane systems that are capable of removing both soluble and particulate pollutants from drinking water.

The project started in August 1997 and was based at CSIRO Molecular Science, Clayton Victoria. A new research scientist (Dr. Tim Carroll) was appointed by CSIRO to work on this project and commenced in November 1997. The project also involved the University of New South Wales (UNSW) Department of Chemical Engineering and the Royal Melbourne Institute of Technology University (RMIT), Department of Chemical and Metallurgical Engineering. The project also collaborated with other CRCWQ&T projects, the Australian Water Quality Centre, Adelaide and the Institut fur Polymerforschung (IPF) in Dresden, Germany. It also supported a number CRC Summer Scholars and visiting overseas students.

The project comprised laboratory and pilot plant experiments using hollow fibre microfiltration membranes to evaluate the membrane filtration performance after a range of pre-treatment systems that included the use of coagulation and/or adsorption processes to maximise NOM removal and minimise membrane fouling. The role of particulate solids and/or coagulated NOM on the fouling and performance of microfiltration membranes was studied at CSIRO and in postgraduate student projects at both UNSW and RMIT. The development and construction of a laboratory scale single fibre microfiltration test rig and a pilot plant scale microfiltration test rig enabled the study of hybrid pre-treatment systems and field demonstrations of the outcomes from the laboratory studies.

Mathematical models based on the fluid dynamics expected within hollow fibre membrane modules were used to predict the performance of single fibre membrane units. The results from the model demonstrated that there are significant design problems with the existing hollow fibre membrane processes and that there is scope to significantly improve membrane performance and to utilise hollow fibre hydrodynamics to minimise fouling of the membrane surface.

The relative benefit of using the hybrid approaches developed in this project was assessed in desk studies compared to alum pre-treatment and based on operating cost data supplied from functioning microfiltration membrane plants.
A collaborative project was undertaken with the IPF, Germany to evaluate the potential for surface modification of hollow fibre polypropylene membranes to prevent fouling by specific components of the NOM present in Australian surface waters. This involved Dr Tim Carroll being based at the IPF in Dresden for 6 months.

A thorough screening of commercially available water treatment coagulants for their suitability before microfiltration of drinking water was undertaken. This was performed both as laboratory scale tests and at the pilot plant scale. The tests concluded that there was very little difference between the aluminium-based coagulants in terms of improving membrane performance. These tests found no quantifiable benefit from using the more expensive pre-polymerised aluminium coagulants (eg poly aluminium chlorohydrate) instead of alum at either scale of testing. None of the iron-based coagulants tested gave as favourable an improvement to membrane performance as alum did.

A fundamental study of floc characteristics on membrane performance showed that floc size has a major effect on membrane flux while floc structure as measured via fractal dimension was of minor importance. The fractal dimension was shown to relate to the compressibility of the filter cake. The implications for membrane filtration are that the filtration of large loose flocs are best performed using low TMP (<10 kPa) while large compact flocs may show better results at high TMP (>10 kPa).

This work also examined the effects of humic acid adsorption on the floc characteristics and membrane filtration. The humic acid was either adsorbed onto preformed hematite flocs or adsorbed onto the hematite and the hematite-humic acid particles flocculated. The adsorption of humic acid onto preformed flocs was a more effective way to remove humic acid from water due to its speed, ability to tailor floc size and structure for flocculation, and the lower resistance and compressibility of the cakes formed. The only apparent advantage of the adsorbing of the humic acid onto the hematite particles before flocculation was a 10 to 20% higher adsorption of humic acid onto the hematite particles.

The effects of micro-particles on microfiltration of water were assessed through dosing of a range of inert and adsorptive particulate materials onto the hollow fibre membranes. Of the particles tested, magnetite, haematite, powdered activated carbon and ion exchange resins dosed onto the MF membranes exhibited minimal resistance to filtration. These particles were then used in combination with coagulation as a pre-treatment before microfiltration. The attachment of alum flocs to these particles was achieved, resulting in protection of the microfiltration membrane from fouling by the floc particles. This combined approach resulted in enhanced membrane throughput compared to direct alum dosing before microfiltration. The most promising hybrid approach was that using 1 g/L of magnetite and an appropriate alum dose to achieve good NOM coagulation. Laboratory tests of this approach demonstrated that membrane throughput could be increased by a factor of about four times compared to alum. However, pilot plant trials of this approach only managed to increase membrane throughput by about 1.5 to 2 times, compared to alum. An economic analysis of the hybrid magnetite/alum approach demonstrated that unless membrane throughput could be increased by over twice that achieved using alum, the benefits were outweighed by the increased operating costs.

Both powdered activated carbon/alum and ion exchange resin/alum hybrid systems could achieve significant levels of NOM removal and also enhance membrane throughput by up to 20 times. However, this enhanced performance was achieved only by using relatively long contact times and high adsorbent doses. These doses and times would make the overall hybrid membrane process expensive to build and operate compared to direct dosing of coagulant before the membrane.

A waste product from the manufacture of ferric sulphate was used as a combined coagulant and particle source. This approach relied on ferric sulphate coagulation of the NOM in the presence of the haematite particles that were also present in the product. The
haematite/ferric solution was dosed directly to the microfiltration membrane and gave similar membrane performance to that achieved using the magnetite/alum approach. As a low cost by-product it should represent a cheap alternative to alum coagulation in microfiltration and warrants further investigation.

The microfiltration of fractionated NOM identified that the main contributor to hydrophobic microfiltration membrane fouling was the low molecular weight neutral hydrophilic fraction. Attempts to identify a suitable process for selectively removing this fraction of the NOM from water before microfiltration were unsuccessful and the idea of modifying the membrane surface to enhance rejection of this fraction of the NOM was investigated. A collaborative project with IPF in Germany built on some expertise they had developed to graft polyelectrolytes to the surface of polypropylene. Preliminary experiments with membranes grafted with cationic or non-ionic hydrophilic polymers demonstrated that fouling rates were 50% lower than for the non-grafted membranes. Rejection of NOM was not compromised and the original membrane was not damaged during the grafting process. However, long term filtration tests indicated that there was no difference in the fouling rates of the grafted and non-grafted membranes, therefore there was no advantage in grafting the membrane surface with these polymers.
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1. Background

In the Australian experience, the strengths of microfiltration (MF) as a water treatment process are

- compactness and low capital cost (no clarifiers or sand filter)
- automated operation and less need for day-to-day operator attendance
- good particle removal (Giardia and Cryptosporidium)
- reduced chemical costs when the feed has low colour
- water quality is independent of flow rate.

The weaknesses are

- poor colour removal
- poor dissolved compounds removal
- backwash water and reject cleaning solution disposal; chemical costs are 50% of operating costs, electricity 16-20%
- short filter run times and large volumes of washwater
- energy costs are high compared to direct filtration, as all the feed has to be pumped

In an endeavour to overcome the problems associated with MF, research on combined systems was proposed, involving a coagulation or adsorption step, followed by membrane separation. The proposed dual systems for drinking water production were simple: soluble natural organic matter, which is not removed by MF and only marginally so by ultrafiltration (UF), would first be converted into a particulate form, enabling its removal by a low pressure microfiltration membrane process.

The research aimed to establish ways of first converting the soluble materials into a particulate form by

- coagulation with a metal salt, which unfortunately increases the solids present when the metal hydroxide is formed
- precipitation with a cationic polymer, acting as a primary coagulant which produces less additional solids
- adsorbing them on clay, with or without a polymer aid
- adsorbing them on metal oxide, with or without a polymer aid
- adsorbing them on powdered activated carbon
- adsorbing them on a finely divided ion-exchange resin.

The project proceeded through the use of laboratory scale experiments to study the attachment of soluble organic compounds onto the surface of selected adsorbents such as clays, powdered activated carbon, ion exchange materials and magnetic micro-particles of iron oxide. The role of polymeric and inorganic coagulants in the coagulation and adsorption of the organic compounds was also studied in laboratory tests using both synthetic model waters and real water samples.

The results of the laboratory tests were used to design suitable pilot plant equipment for continuous trials of the selected pre-treatment processes before microfiltration of some targeted real water supplies.

The outcomes from both the laboratory and pilot plant scale trials were used to evaluate the relative performance characteristics of the combined membrane systems and to determine process economics.
The dominance within Australia of the use of Memcor microfiltration technology has meant that the majority of membranes in use in water treatment are highly hydrophobic, polypropylene hollow fibres with a nominal pore size of 0.2 microns. The configuration of these systems is based on dead end, outside-in filtration through bundles of many thousands of fibres with gas backwashing at frequent, regular intervals for particulate fouling control. As this technology has become almost an industry standard throughout Australia, it was decided that the project would concentrate on the development of hybrid membrane systems based on the use of this hollow fibre microfiltration technology.

1. **Aims:**

1. Develop microfiltration (MF) membrane based technology capable of removing Natural Organic Matter (NOM) from drinking water.
2. Investigate the role of particulate adsorbents with or without the presence of coagulants on the fouling of MF membrane processes.
3. Study the mechanisms of NOM fouling on membrane surfaces.
5. Demonstrate, at the pilot plant scale, hybrid membrane processes for NOM removal on a range of raw water types.

1.2 **Strategies:**

1. Review current international and local practice for the use of membrane processes for NOM removal.
2. Establish and operate bench scale procedures that will allow investigation of the role of particulates and coagulation processes on MF processes.
3. Select suitable adsorbent and/or inert particles (through close collaboration with other relevant CRCWQ&T projects) that can be used in conjunction with MF systems without detriment to membrane performance.
4. Study the role of chemical floc structure on MF membrane performance.
5. Study the effect of particulates in the presence of coagulation processes on the performance of MF processes for NOM removal.
6. Study the role of calcium and NOM on membrane fouling.
7. Design, construct and operate a suitable mobile pilot plant facility that will enable large scale testing and demonstration of the hybrid membrane processes on a range of water types.
8. Develop process design and economic data based on laboratory and pilot plant trials that can be used to advise the Australian water industry on how best to utilise the outcomes from the project in full-scale water treatment plants.

1.3 **Proposed Outcomes**

The ultimate project outcome will be a range of simple, rapid and cost effective processes that can be used in combination with low-pressure microfiltration processes for the removal of dissolved as well as insoluble impurities from drinking water. Thus allowing for improved drinking water quality whilst minimising fouling and increasing the life of membrane processes.

The project milestones that were proposed in the project agreement are listed in Appendix 1.
1.4 Project Staff

The project was a multi-component project, supported by CSIRO Molecular Science, the Royal Melbourne Institute of Technology University (RMIT), the University of New South Wales (UNSW) and the Australian Water Quality Centre (AWQC). The key research staff are indicated in the Table 1, however, there were significant contributions from other staff from each of the organisations indicated above.

Table 1: Key research staff and organisations

<table>
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<tr>
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<td>University of NSW, Randwick, NSW</td>
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<td>Andrea Schæfer</td>
<td>CRCWQ&amp;T PhD scholar - UNSW</td>
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<td>Andrew Lee</td>
<td>CRCWQ&amp;T PhD scholar - UNSW</td>
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<td>Prof. Felicity Roddick</td>
<td>RMIT, Melbourne, Victoria</td>
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<td>Dr John Harris</td>
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<td>Cunli Xiang</td>
<td>CRCWQ&amp;T PhD scholar - RMIT</td>
</tr>
<tr>
<td>Linhua Fan</td>
<td>CRCWQ&amp;T PhD scholar - RMIT</td>
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Other contributions to the project were made at CSIRO by visiting overseas students (Stephan Fellner, Sandra Oh, Annett Rodig, Killian Simbeck and Dirk Vogel) and CRCWQ&T Summer Research Scholars (Natasha Rutherford, Adam Voigt, Rachel Fokkens and Naomi Abraham).

The project collaborated closely with those CRCWQ&T project staff working on both the NOM removal and the polyelectrolytes CRCWQ&T projects

The research extension, which was initiated during the project to look at surface modification of polypropylene membranes, was performed both at CSIRO Molecular Science and at the Institut fur Polymerforschung (IPF) in Dresden, Germany.
2. Research Components

The research performed under this project fell into five main components, these were laboratory tests, pilot plant trials, desk studies, postgraduate student research and collaborative research. Research staff at CSIRO Molecular Science in collaboration with researchers at the Adelaide Water Quality Centre (AWQC) performed the laboratory tests, pilot plant trials and desk studies. University postgraduate research projects were performed at both the RMIT University and at the University of New South Wales (UNSW). Research staff from CSIRO and the Institut fur Polymerforschung (IPF) in Dresden, Germany performed the international collaborative research.

2.1 Laboratory Tests

Aim:

Development of novel hybrid microfiltration membrane processes that allow for enhanced NOM removal in MF whilst minimising membrane fouling. The approach taken has been to combine chemical coagulation with reactive particles (e.g. ion exchange resins, iron oxides or PAC) and present these to hydrophobic hollow fibre MF membranes. The principal idea was to protect the membrane from fouling by NOM and the chemical floc by causing the floc to form around the solid particles before they are presented to the membrane surface.

Research Areas:

- Development of single fibre rig
- Evaluation of role of particulate solids on MF
  - Magnetite
  - Haematite
  - Clays
  - Other metal oxides
- Evaluation of coagulants for use in MF
- Evaluation of adsorbent materials on MF
  - Powdered activated carbon
  - Ion exchange
  - Clay
- Evaluation of hybrid systems
  - Magnetite/alum
  - Haematite/ferric
  - MIEX/alum
  - Powdered activated carbon/alum
- Confirming fouling model development
  - Links to desk studies
- Confirming hydrodynamic model development
  - Links to desk studies
- Determination of role of NOM fractions on MF membranes
  - Harvesting and concentration of NOM from various water sources
  - Fractionation of NOM by charge and hydrophobicity
  - Fractionation of NOM by molecular size
Membrane tests
Identification of fouling fraction
Other attempts to remove/negate fouling fraction
Polymer grafting of membranes to reduce MF fouling
Polymer grafting onto membranes and preliminary fouling response
Extended fouling response of grafted membranes

2.2 Pilot plant trials

Aim:
Demonstration of the most promising hybrid processes that were identified in the laboratory tests, for NOM removal from water. Perform continuous membrane filtration trials using real water samples from a location where the source water is currently treated by the water industry using microfiltration membranes. The purpose of the tests was to demonstrate the technology and develop operating experience, design and economic data in order that the hybrid processes can be fully evaluated.

Research Areas:
Construction of a suitable pilot plant
Demonstration/development of hybrid systems
Magnetite/alum
Haematite/alum
PAC/alum
Assessment of process performance and economics

2.3 Desk Studies

Aim:
To model and assess the performance and fouling characteristics of hollow fibre membrane systems used in water treatment. Develop an understanding of whether the potential processes developed in the research project would be able to technically and economically meet the needs of the Australian water industry.

Research Areas:
Hydrodynamics of hollow fibre membranes
Membrane fouling model
Process performance and economic evaluation

2.4 Postgraduate Student Research Projects

Royal Melbourne Institute of Technology University

Cunli Xiang
Research Aim: To develop a hybrid membrane filtration process for the removal of natural organic matter (NOM), present in Australian surface waters. The process to be studied was based on the use of powdered activated carbon and coagulation in combination with microfiltration membranes.

Linhua Fan
Research Aim: To study the interaction of natural organic matter (NOM), present in Australian surface waters, with microfiltration membrane materials. The different fractions of
NOM have been studied. As well as by size, these fractions include the strongly and weakly hydrophobic, charged and non-charged hydrophilic fractions of NOM. It is anticipated that the fractions of NOM that strongly interact with the membrane surface will be identified and allow the appropriate selection of pretreatment processes to minimise their effects on filtration systems.

**University of New South Wales**

**Andrea Schaefer**

*Research Aim:* To study the interaction of natural organic matter, present in Australian surface waters, with membrane materials. The role of multivalent ions such as calcium and colloidal and micro-particulate species and aggregates in the fouling of NF, UF and MF membranes by NOM was studied.

**Andrew Lee**

*Research Aim:* Chemical dosing before MF processes is common in Australia as a means of enhancing NOM removal by MF membranes. Serious fouling of the membranes can result from the practice, resulting in frequent backwashing and loss of water production as well as the need for high frequencies of chemical cleaning. There is considerable evidence that the type of coagulant used and the manner in which it is used affects the rate of membrane fouling. This indicates that floc structure probably plays an important role in preventing or minimising NOM fouling of MF membranes. The aim of this project is to study the effects of chemical floc structure on the fouling of microfiltration membranes used for the treatment of drinking water.

**2.5 Other Collaborative Research**

*Institut fur Polymerforschung (IPF), Dresden, Germany*

*Research Aim:* To identify whether surface modification of porous polypropylene membranes can reduce the "adsorptive" fouling of these membranes by specific fractions of aquatic NOM.
3. Equipment, Water Sources & Analysis

The project proceeded through a series of laboratory scale tests that were performed at CSIRO Molecular Science, the University of New South Wales, the Royal Melbourne Institute of Technology University and at the IPF in Dresden, Germany. These laboratory tests led to the development of a pilot plant that was designed, built and operated by CSIRO staff to further evaluate any promising pre-treatment approaches identified in the laboratory studies.

3.1 Laboratory Tests

3.1.1 Laboratory scale single fibre MF test rig

The evaluation of membrane performance was based on the use of hollow fibre microfiltration membranes similar to those used commercially in the Australian water industry. New hollow fibre membranes were donated to the project by US Filter Memcor, Windsor, Sydney. The polypropylene microfiltration membrane fibres had an internal diameter of 0.25 mm and a pore size of 0.2 µm. Without any surface modification, the membrane fibres were highly hydrophobic. A membrane test rig (Figure 1) was designed and constructed at CSIRO (CSIRO Internal Report FE-72) and used to test the hollow fibre membranes. Membrane performance tests of various treatment options were performed on the single hollow-fibre rig. The membrane feed water was prepared using standard jar test procedures described below, although the 100 RPM stirring regime was omitted. Feed suspensions were stirred at 250 RPM and the pH controlled at 6.0 (Prominent pump and controller) throughout any membrane performance tests. Coagulant doses were fixed for each sample of water (based on jar tests). The membrane feed pressure and permeate throughput (A&D 6000FG balance) were logged with data acquisition software (Genie), and the permeate flowrate was calculated from the differential throughput.

3.1.2 Water Sources

Water used for control purposes, dilution and making up of standard solutions, as required, was produced by an in-laboratory Milli-Q system, marketed by Millipore. The water used in the laboratory tests was harvested from three main regions of Victoria. In most cases the water used was collected and stored in a refrigerator at 4°C until needed. In the NOM characterisation and fractionation tests water from these sources was concentrated using reverse osmosis (R/O) and the concentrate stored at 4°C until needed.
The raw water sources used in the microfiltration trials were from the East Moorabool River near Anakie and the Maroondah Aqueduct near Yering Gorge, both in Victoria, Australia. The East Moorabool water (Table 2) had a relatively high dissolved organic carbon content (8-12mg/L) and relatively low turbidity (3 - 7 NTU). The Maroondah aqueduct was fed from the Maroondah Reservoir and as such the water had a moderate dissolved organic carbon concentration (2.5-3.5 mg/L), and a very low turbidity (0.6-2.6 NTU).

### Table 2 Main water quality parameters of East Moorabool water

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC (mg/L)</td>
<td>10.2</td>
</tr>
<tr>
<td>UV-254 (1cm cell)</td>
<td>0.182</td>
</tr>
<tr>
<td>pH</td>
<td>7.4</td>
</tr>
<tr>
<td>Ionic strength</td>
<td>4.1 x 10^-3</td>
</tr>
<tr>
<td>Alkalinity (as CaCO_3)</td>
<td>37.3</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>6.5</td>
</tr>
</tbody>
</table>

#### 3.1.3 Analysis

Treated water was filtered through a 0.45µm filter (Selby-Biolab HPLC-certified) and measured for total organic carbon, colour and ultra-violet absorbance.

True colour was measured at 410 nm relative to a platinum-cobalt standard (Pye-Unicam SP6-350 visible spectrophotometer). Ultra-violet absorbance was measured at 254 nm (Shimadzu UV-160 UV-visible spectrophotometer). Total organic carbon was measured by wet chemical oxidation (OI Analytical 1010 Wet Oxidation TOC Analyser).

Turbidity of water samples was measured for unfiltered samples using a Hach XR ratio turbidimeter.

Metal concentrations (aluminium, iron etc.) were determined on acidified (1 to 2 drops of concentrated HCl per 25 mL sample) samples injected into an inductively coupled plasma spectrophotometer (Jobin-Yvon JY24 ICP).

A Coulter Counter Multi-sizer II was used to determine the size distribution of particles below 53 microns. For particle size distributions over this size, standard sieves were used.

### 3.2 Pilot plant tests

#### 3.2.1 Pilot plant construction

The pilot plant was housed within a secure, air-conditioned shipping container and was transportable by truck. The container was fitted with a sink, hot-water service and eyewash station and was supplied with external 3-phase power, which was split off to a single-phase supply at an internal circuit box. All equipment and instruments were securely mounted to a platform within the container, and all feed, product and waste lines ran through threaded sockets in the container wall. The plant comprised four stages:

1. **Contact** - where coagulant and/or particles (eg magnetite or powdered activated carbon) could be dosed and pH controlled
2. **Separation** – where flocculated material and dosed particles could be removed if required
3. **Microfiltration** – where water was pumped through the Memcor MF module
4. **Recovery** – where particles, which were dosed into the water, could be recovered from the separation stage or from the MF backwash water and regenerated for reuse, if necessary.

The process flow diagram is shown in Figure 2. Raw water entered the container through the rear wall, and was fed by a centrifugal pump (Davey Dynaprime, PU2) to the contact stage. The raw water flow rate was controlled by a flowmeter (Kent Veriflux) and control valve (George Fisher). The contact stage consisted of four gravity-fed tanks in series (TA5-
Each tank had a mixer with an independent speed controller, and was dosed by any combination of coagulant, adsorbents, acid or caustic (for pH correction) by any of four dosing pumps (Prominent, PU5-8), with pH control. The treated water was then fed by gravity to a separation stage.

The separation stage consisted of a clarifier (TA9) with conical bottom section, and an overflow weir. A variable-speed agitator was used to prevent outlet blockage by any settled solids. The clarifier could be bypassed if required. The clarifier underflow could be collected and pumped to the recovery stage using a peristaltic pump (Bredel SP15, PU4). The clarifier underflow was pumped to an agitated contact tank and then flowed by gravity to a magnetic drum separator (TA3), where magnetic particles could be recovered and regenerated. Wastewater from the regeneration step flowed from the container under gravity through the rear wall to a 1000 litre buffer tank. Regenerated adsorbents were re-slurried with raw water in an agitated tank (TA4), level controlled by a level switch and solenoid valve. The particles could then be fed back to the contact stage by a peristaltic pump (Bredel SP10, PU3).

The clarified water from the separation stage was fed under gravity to the microfiltration stage, which consisted of a 3m² Memcor microfiltration unit, with automatic air backwash. The microfiltration membrane was fed from an agitated membrane feed tank (TA1) by a variable-speed progressive cavity pump (Mono CP800, PU1). The backwash air was supplied from a regulated gas cylinder and backwash water fed under pressure into an agitated backwash tank (TA2). The backwash water was fed to the magnetic drum separator (TA3) by the clarifier underflow pump (PU4). The permeate left the container through the rear wall via a flowmeter (RS). The temperature and pH of the membrane feed was monitored in the feed tank (TA1).

**Contact stage**

Coagulants, adsorbents, and acid or caustic for pH correction were added in a flexible cascade of four stainless steel tanks. As discussed earlier, the feed to the first tank was
controlled by a flowmeter and control valve, the feed flow rate needed to account for losses from the clarifier underflow and gains from the regeneration tank to produce a net feed flow of 40L/min to the microfiltration plant.

Each tank had a rectangular cross-section (240mm x 220mm x 400mm) for optimum turbulence upon mixing. The liquid level in each tank was maintained at a height of 210mm, which corresponded to a residence time of approximately 15 seconds per tank.

**Solids Separation**
Solids could be separated from the feed water before microfiltration using a high rate clarifier. The clarifier had a cylindrical cross-section (500mm diameter), with a conical bottom, an L-shaped overflow weir, and a subsurface feed line. The rise rate at a plant feed flow of 40 L/min was 12 m/hr. The solids separator could be bypassed and all flow could be fed directly to the microfiltration unit, if required.

**Membrane module**
The heart of the pilot plant was a 3m² Memcor microfiltration unit. The membranes were housed in three cartridges, each containing approximately 10,000 polypropylene hollow-fibres with a nominal 0.2 µm pore size. In normal operation, the membranes are run in dead-end mode (MV2 closed).

During the backwash cycle, pneumatic valves on the filtrate and recirculation lines close (PV1A and PV2) and pneumatic valves on the drain and exhaust lines open sequentially (PV1A and PV2A respectively). The high-pressure air solenoid valve opens (SVH) and solids deposited on the membrane during filtration are expelled to the backwash tank (TA2). The rewetting cycle follows the backwash cycle automatically, but could be initiated manually. All pneumatic valves close, and the high-pressure air solenoid valve opens. Filtrate is forced back through the membrane at 600kPa. All lines are then air-blown before filtration resumes. A programmable logic controller controls filtration, backwash and rewet cycles. Chemical cleaning was required when performance could not be recovered by backwashing alone. The cleaning agent used was 2% Memclean (a sodium hydroxide-surfactant solution). Citric acid and hydrogen peroxide were also used to chemically clean other contaminants from the membrane surface, when required.

The pure water flux achieved by the Memcor plant was approximately 20 L/hr/kPa/m². This corresponded to a flow rate of 40 L/min at the minimum operating pressure of 40kPa. This pure water flow rate was the basis for both line and equipment sizing.

**Monitoring and control**
Periodic sampling of the feed and filtrate streams enabled off-line analysis and monitoring of water quality. The water was analysed for total organic carbon concentration, ultra-violet absorbance (at 254nm), turbidity and colour.
The microfiltration performance was monitored continuously, and data logged automatically using Genie software, and Adams acquisition modules, as shown in Figure 2. The feed and filtrate flow rates, the feed, filtrate, and recirculation pressures, and the pH and temperature of the membrane feed were each logged in a data file. The microfiltration performance was reported as filtrate flux (filtrate flow rate per unit transmembrane pressure and membrane surface area). All instruments were configured for 4-20mA or 0-100mV output, and had both local displays (except for temperature) and PC console displays.

### 3.2.2 Pilot plant operation

The membrane pilot plant was set up at the Melbourne Water Corporation’s (MWC) pumping station site at Yering Gorge, on the banks of the Yarra River, close to Sugar Loaf Reservoir and the Winneke Water Treatment Plant. MWC provided access to the site as well as the power and water necessary to run the pilot plant. The pilot plant treated water that flowed from the Maroondah Reservoir at Healesville to the Yering Gorge pumping station, via the open Maroondah aqueduct. This water source was the same as that accessed for treatment by MWC’s microfiltration membrane plant at Yarra Glen.

The raw water from the aqueduct generally had a moderate dissolved organic carbon content (TOC = 2.5-3.5 mg/L), and a low turbidity (0.6-2.6 NTU). However, during the late summer months, algae formation within the aqueduct was observed and this contributed up to about a four-fold increase in raw water turbidity. At this time, operators at the Yarra Glen plant observed severe fouling of their microfiltration membrane units by the algae and the volume of backwash water produced, usually exceeded the design capacity and resulted in frequent plant shutdowns.

A 25 mm polypropylene pipe connected the pilot plant to the aqueduct and allowed raw water to siphon into the plant. As the aqueduct was located about 50 metres above the level of the pilot plant, there was sufficient static head to allow the pilot plant to operate without the need for the feed pump (PU2).

The membrane unit was run at a constant permeate flux of 360 L/m$^2$h, and an initial transmembrane pressure (TMP) of 40 kPa. The TMP increased as fouling proceeded and was monitored and logged against run time. The membrane was backwashed to a waste tank at 60 minute intervals using 600 kPa air. Once the TMP of the backwashed membrane reached a value of 180 kPa the membrane was chemically cleaned with a proprietary cleaning solution (Memclean), mixed with hydrogen peroxide. The membrane was then flushed with pure water (generated on site by reverse osmosis of the raw water) until the initial TMP of 40 kPa was achieved. Turbidity and UV absorbance (254 nm) were measured on both feed and permeate.

A number of membrane trials were performed using the membrane pilot plant. Each trial was generally performed for about six hours, thus allowing for a number of backwash cycles during each trial. This mode of operation allowed for start-up and shutdown of the pilot plant each day, as staff had to travel to the site each day from Clayton.
4. NOM Fouling of Microfiltration Membranes

The role of natural organic matter in the fouling of microfiltration membranes was evaluated in a series of laboratory tests performed at CSIRO and also formed the basis of a postgraduate student research project at RMIT.

Polyelectrolyte-grafted MF membranes were developed and evaluated in an attempt to control fouling of hydrophobic hollow fibre membranes by NOM (Publications 6 and 7). CSIRO Molecular Science staff, in collaboration with the Institut für Polymerforschung (IPF), Dresden, Germany, performed the research both at Clayton and in Dresden. The IPF had previously developed a patented method for chemically altering the surface properties of polypropylene to enable grafting of various organic compounds onto the surface of the polymer (Reference 4), and we were interested to see whether it was possible to take the surface modification a step further by grafting polyelectrolytes onto polypropylene MF membranes to control and/or influence electrostatically-driven fouling.

4.1 Method

4.1.1 Membrane fouling by NOM

Raw water was harvested from the Moorabool River near Anakie, Victoria. The water had low turbidity (3.9NTU), low salinity and hardness, but a high dissolved organic carbon (DOC) content (9.0mg/L). The raw water was concentrated to a DOC of approximately 500mg/L by reverse osmosis, and fractionated according to an established ion-exchange procedure (Reference 1). The raw water concentrate was filtered through a 0.45µm membrane, adjusted to pH 2, and fed onto a Superlite DAX-8 resin, which retains strongly hydrophobic substances (e.g. humic and fulvic acids). This fraction was eluted with NaOH and acidified on an IRC-120 resin. The unadsorbed concentrate was fed onto an Amberlite XAD-4 resin, which retains weakly hydrophobic substances. This fraction was eluted with NaOH and separately acidified on an IRC-120 resin. The unadsorbed hydrophilic (non-humic) concentrate, attributed to proteins, amino acids and carbohydrates, was fed onto an Amberlite IRA-958 resin, which retains charged material. This fraction was eluted with a NaOH/NaCl mixture. The remaining neutral material was not retained by any of the resins.

Microfiltration experiments were carried out on single polypropylene hollow-fibre membranes using the filtration apparatus shown in Figure 1. Fibres were wet and degreased with ethanol, and flushed thoroughly with ultra-pure water before use. The feed was pumped onto the membrane from a stirred tank using a peristaltic pump. The feed was forced through the fibre wall under pressure, to emerge as permeate from the open ends. The permeate was collected in a vessel mounted on an analytical balance. Feed pressure was monitored with a pressure transducer. The signals from the analytical balance and pressure transducer were processed to calculate the permeate flowrate as a function of permeate throughput. Experiments were performed at pH 6.

The four Moorabool NOM fractions were separately reconstituted to their respective TOC concentrations in the raw water. Calcium and sodium concentrations of each fraction were corrected to the raw water values to eliminate electrostatic-mediated contributions to fouling. The four different fractions were then passed through the membrane fibres and the flux versus throughputs determined for each fraction individually (CSIRO Internal Report FE-80).

4.1.2 Role of membrane material in NOM fouling

The aquatic NOM used was isolated from 600L of raw water from East Moorabool Reservoir, Victoria using reverse osmosis (RO) equipment and 0.45 µm MF membranes. Some general characteristics of this water are shown in Table 2. NOM isolates were fractionated by the established XAD-8/4 procedures (Reference 1) to give four fractions - very hydrophobic acids; slightly hydrophobic acids; hydrophilic charged components and hydrophilic neutral components. A synthesised NOM solution was prepared by mixing the four fractions in the same proportion as found in un-fractionated NOM. The ionic strength
was adjusted using 1M NaCl and solution pH adjusted upwards and downwards by the addition of 1M NaOH and 1M HCl, respectively. All chemicals were analytical grade and purchased from Ajax, Australia. Pure water was generated from a laboratory research grade water system (MODULAB™, XLPV 01002).

Table 3. PVDF microfiltration membrane characteristics

<table>
<thead>
<tr>
<th>Parameter</th>
<th>GVWP</th>
<th>GVHP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal pore size [µm]</td>
<td>0.22</td>
<td>0.22</td>
</tr>
<tr>
<td>Material</td>
<td>modified PVDF (hydrophilic)</td>
<td>PVDF (hydrophobic)</td>
</tr>
<tr>
<td>Protein binding capacity [µg/cm²]</td>
<td>4</td>
<td>150</td>
</tr>
<tr>
<td>Pure water flux (50 kPa) [L/m²/h]</td>
<td>2230 ± 130</td>
<td>2280 ± 180</td>
</tr>
<tr>
<td>Measured median pore size [µm]</td>
<td>0.45</td>
<td>0.45</td>
</tr>
<tr>
<td>Mean thickness [µm]</td>
<td>125</td>
<td>125</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>70</td>
<td>75</td>
</tr>
<tr>
<td>Surface charge at pH 8 [mV] *</td>
<td>-21.1</td>
<td>-9.8</td>
</tr>
</tbody>
</table>

Two types of 0.22 µm polyvinylidene fluoride (PVDF) membranes (GVWP and GVHP, Millipore) were tested in the experiments (Publications 8 & 9). The characteristics of the experimental membranes are shown in Table 3. MF experiments were carried out using flat plate membranes in a stirred cell (Amicon 8050, effective membrane area 13.4 cm²) connected to a feed reservoir. The transmembrane pressure was regulated using nitrogen gas. The operating pressure was 50 kPa and the stirring speed was set to 300 rpm. All experiments were conducted at room temperature (22 ± 2 °C). For each run, a fresh membrane was used. The permeate flux was determined using a top-loading electronic balance (Sartorius, BP6100) connected to a computer for continuous recording of data.

A UV/Visible spectrophotometer (Philips, PU 8620) was used to measure UV absorbance of the NOM solutions. TOC was measured using a TOC analyser (I-O-Analytical Model 1010) equipped with an automatic sample injector. Surfaces of the fresh and fouled membranes were examined by SEM (Philips XL30) as a basis of comparison for the investigation of membrane fouling.

4.1.3 Evaluation of adsorbent materials

The outcomes of the CRCWQ&T project looking at technologies for the removal of NOM from water was consulted for the most likely candidates from the range of possible adsorbents that could be used for pre-treatment of water to maximise NOM removal. Of the adsorbents tested, it was felt that both magnetic ion exchange resin MIEX™ and powdered activated carbon were probably the best to evaluate for membrane pre-treatment.

The adsorption of the hydrophilic neutral NOM fraction by various adsorbents was determined in a number of laboratory scale jar tests. This was attempted after it became apparent that the NOM remaining after alum coagulation and floc separation still led to membrane fouling. Powdered polypropylene and finely chopped hollow fibre polypropylene membranes were both used in jar tests to determine whether there was significant adsorption of the neutral hydrophilic NOM fraction by these materials. Powdered activated carbon, ion exchange resin (MIEX) and clay were also used in jar tests to determine whether this specific NOM fraction could be selectively adsorbed from the water.

4.1.4 Microfiltration membrane surface modification

Some preliminary experiments were undertaken on modified membranes sent to CSIRO by IPF to determine whether the approach had any potential for success. Following these initial tests, Dr Tim Carroll was sent to Germany for six months to work in the IPF laboratories to develop and evaluate the grafted membranes using NOM from water harvested in Australia.
The raw water source was the Moorabool River near Anakie, Victoria, Australia. At the time of harvesting, the water had a dissolved organic carbon (DOC) concentration of 9.0 ppm, a turbidity of 4.3 NTU, a pH of 7.4 and a calcium concentration of 10 mg/L as CaCO₃ equivalents. The NOM was extracted from the water and concentrated to approximately 50 times its original concentration by reverse osmosis. It was then fractionated into strongly hydrophobic, weakly hydrophobic, charged and uncharged fractions, as described earlier. These fractions and a sample of the concentrated raw water were shipped to Germany where they were reconstituted back to their original “raw water” concentrations using MilliQ water. The raw water was filtered both untreated and after coagulation pre-treatment with alum. In the former case, the pH was adjusted to 6.5 before filtration. In the latter case, alum was dosed at 5.0 mg/L (as Al³⁺), the pH was adjusted to 6.5, and the water was filtered after 5 minutes coagulation time. The effect of water hardness was investigated by adding calcium chloride to the raw water (adjusting to pH 6.5) at concentrations of 100 and 350 mg/L as CaCO₃ equivalents.

The microfiltration membranes used were polypropylene hollow fibres with a nominal pore size of 0.2 µm, an internal diameter of 250 µm, an outer diameter of 550 µm, a length of 0.9 m, and a nominal surface area of 7 cm². These membranes were modified by grafting with positively charged, negatively charged or non-ionic hydrophilic polymers to form positively charged, negatively charged or non-ionic (respectively) charged surface layers using the technique developed by IPF (Publication 6).

Microfiltration experiments were carried out on the original and graft-modified single polypropylene hollow-fibre membranes. Filtration through the fibre was from outside to inside. Fibres were opened at both ends, sealed by threading the ends though a silicone septum and prepared by wetting with ethanol and flushing thoroughly with pure water (MilliQ). The feed water was forced through the fibre under nitrogen pressure of 50 kPa, and the permeate was collected from the opened ends in a container placed upon an analytical balance. The signal from the balance was processed to calculate the permeate flux as a function of permeate throughput.

4.2 Results

4.2.1 Membrane fouling by NOM

The TOC of each of the four Moorabool NOM fractions extracted from the raw water concentrate are shown in Table 4. The TOC distribution for Moorabool water was approximately 1/3 strong hydrophobic, 1/6 weak hydrophobic, 1/3 charged hydrophilic, and 1/6 neutral hydrophilic.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>TOC (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strongly hydrophobic</td>
<td>3.1 (34%)</td>
</tr>
<tr>
<td>Weakly hydrophobic</td>
<td>1.6 (18%)</td>
</tr>
<tr>
<td>Charged hydrophilic</td>
<td>3.0 (33%)</td>
</tr>
<tr>
<td>Neutral hydrophilic</td>
<td>1.4 (15%)</td>
</tr>
<tr>
<td>Unfractionated</td>
<td>9.0 (100%)</td>
</tr>
</tbody>
</table>

The decline in permeate flow rate with permeate throughput during microfiltration of the four reconstituted Moorabool NOM fractions is shown in Figure 4. The decline for the raw water pre-filtered through a 0.2µm membrane is also shown for comparison. The rates of fouling were relatively low for the strong hydrophobic, weak hydrophobic, and charged hydrophilic fractions (decline in permeate flow rates of approximately 16% after 800g was filtered). The rates of fouling were significantly faster for the neutral hydrophilic fraction and the pre-filtered raw water (40% and 50% respectively after 800g was filtered).
Linhua Fan (RMIT) studied the mechanism of fouling by the hydrophilic neutral fraction of NOM on flat plate hydrophobic GVHP membranes (Publication 9). The flux decline caused by the neutral fraction at 5 mg/L of DOC was severe with only 8% of the initial flux remaining at the end of the filtration experiment. Water containing only 0.4 mg/L of the hydrophilic neutral DOC (the same concentration as found in the unfractionated NOM) induced almost the same rate and extent of flux decline as the reconstituted raw water. Pre-filtration of the neutral fraction using a 30 kDa membrane significantly reduced the flux decline compared to the non-prefiltered neutral fraction. The most severe flux decline in this case was mainly attributed to high MW neutral compounds (> 30 kDa), which accounted for about 30% of the DOC in the raw water used. Calcium analysis showed that 7% of the Ca$^{2+}$ in the neutral fraction was retained by the 30 kDa membrane. This suggests that Ca$^{2+}$ is interacting with polar groups on the hydrophilic neutral compounds to form large molecules/colloids, but the reactions involved are not clear (Publication 22). These results support the hypothesis made by Cho et al. (Reference 6) that the larger hydrophilic fractions of NOM without significant ionisable functionality were responsible for significant membrane fouling.

The membrane lost more than half of its initial permeability after 30 minutes of filtration of the 30 kDa-prefiltered neutral fraction, suggesting that the small neutral compounds are also capable of causing considerable flux decline. Research performed at CSIRO (Publication 3) demonstrated that the NOM remaining after coagulation pre-treatment was mostly the smaller sized hydrophilic neutral compounds, and adsorptive fouling was the most likely fouling mechanism for these compounds on a hydrophobic polypropylene hollow-fibre membrane.

The results of both these studies suggest that the mechanism of fouling by the hydrophilic neutral fraction is a combination of adsorption of small molecules on the membrane pore wall and pore blockage by colloidal organics within the membrane structure.

### 4.2.2 Role of membrane material in NOM fouling

The effects of the hydrophobicity of the membrane surface (Publications 8 and 9) and the solution pH on relative membrane flux are shown in Figure 5. The hydrophilic GVWP membranes fouled at a much lower rate than the hydrophobic GVHP membranes during microfiltration of the reconstituted East Moorabool water. This suggests that membrane hydrophobicity is a critical determinant of fouling by NOM. The fouling rate of GVHP was higher at pH 4.1, which was most likely due to increased aggregation of the NOM at this
pH, resulting in particulate fouling of the membrane.

4.2.3 Evaluation of adsorbent materials

The use of adsorbent materials for NOM removal is discussed in more detail in Section 7. However, none of the adsorbent materials tested showed any appreciable capacity for the neutral hydrophilic NOM fraction. Only powdered activated carbon at doses greater than 1 g/L showed any capacity for this specific NOM fraction, removing 25% of these organics, after 24 hours of contact. MIEX resin, montmorillonite clay, magnetite, powdered polypropylene and chopped polypropylene membrane fibres all removed none of the organics in this specific fraction of the NOM.

Microfiltration membrane surface modification

A number of experiments were performed (Publications 6 and 7) with the different surface modified membranes. These experiments showed that both the positive and neutral surface modification approaches yielded less improvement to membrane performance than the anionic grafts. The membrane performance using the negatively charged surface modified membranes was therefore studied in more detail. The flux declines versus throughput for Moorabool water, filtered through both original and modified membranes (negative surface charge), with and without coagulation pretreatment, are shown in Figure 6. The flux decline was most pronounced for the untreated water filtered through the original membrane, dropping by 60% after 500 L/m² throughput. Pretreatment with alum reduced the flux decline for the original membrane to 30% after 500 L/m² throughput. This reduction was due to the effect of flocculation on particle size and cake resistance (Publication 6).

The initial fluxes for the modified membranes (7.2 % w/w graft yield) were approximately 60% lower than for the original membranes. However, the flux increased upon filtration, by 75% and 125% for the untreated and alum-treated water respectively. In the former case, the flux reached a maximum at 100 L/m² throughput, while in the latter case, the maximum flux was at 250 L/m² throughput. In both cases, the flux declined at higher throughputs. In the untreated water case, the flux was consistently higher for the modified membrane than for the original membrane after the maximum flux of the former was reached. This enhancement corresponded to an increase in throughput of approximately 100% for a given flux over the range investigated. However in the alum-treated water case, the fluxes through the original and modified membranes were similar after the maximum flux was reached.
The flux declines versus throughput for raw and artificially-hardened Moorabool water filtered through modified membranes are shown in Figure 7. In all cases, the initial flux was lower than for the original membranes and the flux increased initially but declined at higher throughputs, as described earlier. As the calcium concentration increased, the flux enhancement was reduced, and the throughput at maximum flux was also lowered. The flux at a given throughput was consistently highest for the softest water.

Figure 6: Flux decline with throughput for untreated water through original (●) and modified (○) membranes and alum treated water though original (■) and modified (□) membranes.

Figure 7: Flux decline with throughput for soft (○), moderately hard (□) and hard (△) surface water through modified membranes.
4.3 Discussion

The neutral hydrophilic component of NOM caused more severe fouling of the polypropylene microfiltration membrane than hydrophobic or charged components. In previous work on the same Moora bore NOM fractions, the size distributions of the four NOM fractions were measured by size exclusion chromatography (Reference 2). These results showed that the NOM in the neutral hydrophilic component was smaller in size than in the other three fractions. NOM may foul a microfiltration membrane by either precipitating at the membrane surface, or adsorbing within the pore space. However, a precipitative mechanism would favour fouling by large hydrophobic NOM (e.g. humic or fulvic acid), as these substances have lower solubility limits, greater tendency to aggregate, and lower diffusion rates from the membrane surface than do the small hydrophilic NOM. Therefore, the possibility of an adsorptive mechanism should not be excluded (Publication 3 and CSIRO Internal Report FE-80).

The fouling of microfiltration membranes by neutral hydrophilic NOM has several implications for microfiltration performance. The concentration of neutral hydrophilic NOM in the feed water may be a better indicator of potential fouling than the total NOM concentration. Membrane chemical cleaning may be more effective if the chemical agent selected specifically targets these neutral hydrophilic substances.

A combined coagulation-microfiltration process may not reduce NOM fouling, because aluminium or iron salts preferentially coagulate large, charged, hydrophobic NOM (Reference 3). Coagulation in combination with an adsorption step specific to these small neutral substances would be an ideal pre-treatment before microfiltration. However, of the adsorbents tested, none showed any appreciable capacity for this fraction of the NOM apart from activated carbon. The dose of powdered activated carbon needed to effect a significant reduction in these organics would be uneconomically high for continuous dosing into any water treatment process.

The small, neutral, hydrophilic NOM should be readily susceptible to biodegradation. Why this has not occurred within the reservoir during the long periods that the water has been stored is not obvious. One possible reason could be that these specific organics are constantly being produced during the biodegradation of other organic material within the reservoir.

A membrane material that reduces fouling by small, neutral, hydrophilic NOM may give improved microfiltration performance. This would be particularly likely in a combined coagulation-microfiltration process, where most of the residual NOM is comprised of neutral substances. This was demonstrated in the experiments where hydrophilic membranes were compared to hydrophobic membranes for the filtration of NOM containing water. The hydrophilic membranes, although still susceptible to fouling, did foul at a lower rate than the hydrophobic membranes.

These results justify looking for membrane surface modification techniques that target the small neutral hydrophilic NOM compounds. NOM fouling of non-ionic and cationic hydrophilic grafted polypropylene membranes resulted in rates of flux decline up to 50% lower than ungrafted polypropylene. Anionic hydrophilic grafts had lower initial fluxes, but the flux increased by up to 140% at high graft yields during filtration, assisted by the presence of multivalent ions in the water.

The performance of the modified membranes can be understood in terms of the effect of specific feed water properties upon the permeability of the grafted layer. The initial flux is lower for the modified membranes because the grafted polyacrylic acid chains partially occupy the membrane pore space, increasing the hydraulic resistance to filtration. The chain conformation varies with pH, depending on the degree of polyacrylic acid dissociation and the resultant charge density. The polyacrylic acid chains are highly negatively charged at pH 6.5, and the chains are extended rather than coiled as a result (Publication 6). The grafted layer is therefore relatively thick initially. However, as filtration proceeds, multivalent counterions, such as calcium or magnesium, can bridge the charged groups on the
polyelectrolyte chains to generate a more coiled conformation. NOM-polyelectrolyte bridging by calcium is also possible. The graft layer becomes thinner, and the permeability increases (Publication 6).

The modified membranes can exhibit a lower rate of flux decline with throughput than the original membranes if the increase in permeability of the grafted layer counteracts the flux decline due to fouling by the feed water. The performance of the modified membranes depends upon raw water characteristics, pretreatment regimes and the polyelectrolyte graft yield. A soft water may produce a gradual long-term flux increase whereas a hard water may produce a sharp short-term flux increase. On the other hand, the flux decline due to fouling is typically determined by particulate matter concentration and physical properties of the water (as well as membrane properties etc.). However such a flux decline may be reduced by coagulation pretreatment if the cake resistance of retained particulate matter is lowered. The interplay of all of these features will determine the potential for improved membrane performance by polyelectrolyte graft modification.

4.4 Conclusions

Fouling of polypropylene microfiltration membranes by NOM is more severe for the hydrophilic, neutral fraction of NOM than for hydrophobic substances such as humic or fulvic acids. The hydrophilic neutral fraction of NOM may contain organic compounds such as carbohydrates and polysaccharides and in the waters studied here contained appreciable quantities of calcium and iron; however, the exact nature of molecules responsible for fouling has not been identified. This fraction of NOM was not significantly removed by conventional treatment approaches such as coagulation and sedimentation. Removal of this fraction using common water treatment adsorbent materials was also ineffective.

The removal of this fraction of the NOM before membrane filtration has many implications for plant design, operation, and performance. Further work is required to evaluate the mechanism by which this fraction of the NOM fouls hydrophobic membranes. Research is also recommended into the identification of alternative adsorbent materials that may be specific to the neutral hydrophilic organics responsible for membrane fouling.

It is possible to minimise the flux decline caused by NOM fouling of a microfiltration membrane either by selecting membrane materials with a hydrophilic surface or by surface modification of hydrophobic membranes.

Charged and non-charged hydrophilic polymers grafted as a flexible layer onto a microporous polypropylene hollow fibre resulted in a membrane whose flux depended on polymer conformation, as controlled by properties of the feed stream such as pH and multivalent counterions. Non-ionic and cationic hydrophilic grafts had rates of flux decline, caused by NOM fouling, up to 50% lower than ungrafted polypropylene. Anionic hydrophilic grafts had lower initial fluxes, but the flux increased by up to 140% at high graft yields during filtration, due to multivalent ions in the water. These surface modified membranes can filter a NOM-containing surface water for extended periods without any flux decline due to NOM fouling or without compromising permeate quality. These tailor-made modified membranes function by increasing the grafted-layer permeability to counteract fouling. Rejection is not compromised, as the original membrane is not damaged during modification. It may be possible to control performance for a particular feed source by matching graft polymer and graft yield to source pH and counterion concentration (e.g. hardness).
5. Particles and Microfiltration

5.1 Method

5.1.1 Role of particulates in membrane fouling

Andrea Schaefer (UNSW) performed experiments (Publications 10, 11 and 12) using stirred cell equipment, polymeric membranes and synthetic surface water containing natural organics, inorganic colloids and their aggregates, and cations. The study focussed on the analysis of fouling in microfiltration, ultrafiltration and nanofiltration membrane processes. Pre-treatment with ferric chloride was performed in order to study the effects of coagulation and aggregate formation on the fouling of all three of these polymeric membrane classes, during drinking water treatment.

Andrew Lee (UNSW) continued this research (Publication 17) using haematite floc to study the relationship between floc characteristics and MF performance. Floc properties were observed using Small-Angle Laser Light Scattering (SALLS). MF experiments on the floc suspension were performed to allow filtration performance to be analysed. An objective of this study was to establish a floc structure relationship for flocculated feed in water and wastewater treatment instead of the highly empirical Carman-Kozeny equation for dead-end MF.

Water used in the studies was harvested from Moony Moony Dam in NSW, filtered by microfiltration then concentrated using reverse osmosis and freeze drying.

5.1.2 Selection of suitable particles for microfiltration

The microfiltration performance of a variety of particulate materials (CSIRO Internal Reports FE-72, FE-76 and FE-77) including clays (kaolinite, bentonite, montmorillonite and ball clay), activated carbon, MIEX resin, and three magnetite grades (Sirofloc, Bayer and pigment) were evaluated. Each adsorbent was filtered as a 100mg/L suspension in MilliQ water. Membrane performance was monitored as permeate flowrate (flux) as a function of throughput. For comparative purposes, the microfiltration performance of pure alum and polyaluminium chloride flocs was also investigated. The flocs were formed in MilliQ water at 100mg/L of coagulant (as alum or aluminium chloride), adjusting pH to 6.0 and 7.0 respectively. The extent of performance recovery by gas backwashing was investigated in selected cases.

![Figure 8: Particle size distributions of particulate material used in membrane tests](image)

The size distributions of the four clays are shown in Figure 8(a). Montmorillonite and ball clay have a mean particle diameter of 6µm. Kaolinite has a mean particle diameter of...
10 µm, and bentonite has a mean particle diameter of 18 µm. The size distributions are relatively broad in all cases. The size distributions for the magnetite grades are shown in Figure 8(b). Sirofloc grade had a mean particle diameter of 26 µm. Pigment grade had a mean particle diameter of 6 µm, and Bayer grade had a mean particle diameter of 2 µm, with an appreciable fraction below the nominal 0.2 µm membrane cut-off. The activated carbon (Aldrich) has a mean particle diameter of 39 µm, and the MIEX resin (D50) has a mean particle diameter of 176 µm.

5.2 Results

5.2.1 Role of particulates in membrane fouling

All the polymeric membrane processes (Publication 14) used for water treatment that were tested could remove significant amounts of natural organic matter from water. Pre-treatment with ferric chloride was required to achieve significant organic removal with MF and high molecular weight cut-off ultrafiltration (UF) membranes.

Figure 9 shows that specific resistance increases with fractal dimension (Fig. 9a) and reduces with floc size (Fig. 9b). Cake compression may influence the MF performance because flocs with a fractal dimension between 2.0 and 2.1 are likely to form highly compressible cakes. A focused ion beam (FIB) milling method is being used to observe cake morphology. The results give qualitative information about floc deposition and the compression mechanism. The research team at UNSW is undertaking further research to study floc size distribution and cake compression and morphology.

5.2.2 Selection of suitable particles for microfiltration

The microfiltration performance of kaolinite, montmorillonite, bentonite and ball clays were compared to MilliQ water in Figure 10(a). The flux decline observed for montmorillonite and bentonite was severe, with the flux dropping to 50% of the initial value after processing approximately 70 g of the suspension (7 mg of the clay). The flux decline for kaolinite was considerably lower. 2000 g of the suspension (200 mg of the clay) was filtered before the flux declined to 50% of the initial value. The flux decline for ball clay was minimal, at approximately 8% of the initial value after 2000 g of the suspension was filtered, dropping to 22% after 5000 g was filtered (500 mg of the clay).

The microfiltration performance of flocculated coagulants (polyaluminium chloride (PACl) and alum) in MilliQ water is shown in Figure 10(b). The flux decline for PACl flocs (at pH=7) is severe, with the flux dropping to 50% of the initial value after processing approximately 1 mg (as AlCl₃) of the flocs. The flux decline for alum flocs (at pH=6) was slightly better, with approximately 70 mg of the flocs processed before the flux dropped to 50% of the initial value.
The microfiltration performance of the three grades of magnetite, MIEX resin and activated carbon are shown in Figure 10(c). The performance of MIEX resin falls between that of kaolinite and ball clay. The flux decline was approximately 19% after 2000g of the suspension was filtered, dropping to 37% after 5000g was filtered. However, in the case of activated carbon and all magnetite grades, the flux decline was minimal and comparable to the filtration of MilliQ water.

The backwashing performance of ball clay and montmorillonite were compared to MilliQ water in Figure 10(d). There was some flux decline on rewetting due to membrane compression in the first backwash-rewet cycle (MilliQ). However, in no case was flux recovery complete. Even in cases where flux was recovered, the extent of recovery was lower for the second backwash-rewet cycle than for the first.

5.3 Discussion

5.3.1 Role of particulates in membrane fouling

In basic terms, two resistances govern the rate at which a suspension is filtered through a microporous membrane. The membrane offers a resistance to filtration that is overcome by feeding under pressure. As a suspension is filtered, the particles retained form a cake on
the membrane surface. The hydraulic resistance of this cake may also contribute to the filtration resistance. The ideal particle will be one that contributes no resistance to filtration above that offered by the membrane itself. The hydraulic resistance contribution of a filter-cake can manifest itself by a decline in membrane flux with throughput. (In practice, the pressure is increased to keep the flux constant, raising operating cost). Hydraulic resistance will depend on particle size, cake porosity, particle shape (fractal dimension and compressibility).

Flocs with a fractal dimension of about 2.0 seem to show more complicated behaviour than mono-dispersed spherical particles (fractal dimension approaching 3.0) in cross-flow channels. Floc movement in cross-flow microfiltration is little understood and the fractal dimension effect will be studied further. In addition, the fractal dimension dependence during the membrane backwash process will be examined further at UNSW.

5.3.2 Selection of suitable particles for microfiltration

The hydraulic resistance offered by different clays of similar particle size varied considerably. The clays investigated, in order of increasing resistance, were ball clay > kaolinite > bentonite > montmorillonite. This trend might be attributable to potential for swelling. Montmorillonite swells in water to expose an effective surface area of approximately 700m²/g, whereas kaolinite is non-swallowable, and has an effective surface area of approximately 20m²/g. Deposition of a swellable clay on the membrane surface may result in a highly compressible cake of gelatinous texture, which would be have very low porosity. Non-swellable clay may form a cake retaining the characteristics of the original particles, resulting in a higher porosity. The different cake characteristics would cause different flux decline rates. Bentonite is impure clay, a mixture of montmorillonite with kaolinite, with a flux decline rate comparable to montmorillonite. Ball clay is a disordered kaolinite. However it has a lower hydraulic resistance as a cake in water than kaolinite, and presents the most promising option to date for application of clay to the microfiltration of drinking water.

The hydraulic resistances of all magnetite grades and activated carbon were negligible compared to the resistance offered by the membrane. The hydraulic resistance offered by the cake of magnetite particles was independent of particle size (relative to membrane resistance) and was negligible even for the Bayer grade, which was close in size to the membrane pore size. The incompressibility of the magnetite would appear to be more significant than the porosity. A cake of activated carbon particles is also relatively incompressible, and this was reflected by the low hydraulic resistance (relative to membrane resistance) observed in these tests. Magnetite and activated carbon would be ideal particles for microfiltration of drinking water from a hydraulic-resistance perspective.

The MIEX resin beads that were tested had fine particles of iron oxide associated with them that appeared to cause fouling of the membrane surface. Despite repeated cleaning of the resin in the laboratory, these fine particles were always present in the MilliQ water/resin mixture that was pumped to the membrane during the flux decline experiments. As a result, the hydraulic resistance fell between that of kaolinite and ball clay, even though the MIEX resin particle size was considerably larger than either clay.

Flux recovery by gas backwashing was reasonably successful. However, there was a long-term loss in performance and sequential backwashing became progressively less effective. This feature was observed for ball clay and montmorillonite, as well as for pure alum flocs. However, on the basis of microfiltration investigations reported here, the flux decline during filtration has a much greater impact on performance than potential for flux recovery by gas backwashing. In the case of both ball clay and alum flocs, the flux loss after the first backwash was comparable to the corresponding MilliQ flux loss (caused by compression of the membrane at rewet pressure). However, in the case of montmorillonite, flux loss after the first backwash was considerable. It can be speculated that flux recovery by gas backwashing may be influenced by the nature of the deposited cake. Montmorillonite forms a compressible cake of gelatinous texture. This may be more difficult to remove from the membrane surface than the ball clay cake, which was closer in texture to the individual clay.
particles. In any case, both flux decline by filtration and flux recovery by backwashing showed similar trends in the cases investigated. Furthermore, if flux decline is severe, (as for example in the case of montmorillonite) the benefit offered by backwashing is minimal. The frequency of backwashing to maintain a reasonable flux would be relatively high, compromising productivity and yield.

5.4 Conclusions

Fouling mechanisms for NF, UF and MF membrane processes (Publications 11 and 17) showed that the crucial parameters affecting performance were aggregate characteristics (fractal structure, stability, organic-colloid interactions), solubility of organics and calcium, and hydrodynamics. In MF, fouling by pore plugging was most severe. Variations in solution chemistry changed the aggregation state of the colloids and/or natural organic matter and dramatically affected rejection and fouling behaviour. UF membrane fouling was mainly influenced by pore adsorption and could improve natural organic matter rejection significantly. Coagulant addition shifted the dominant fouling mechanism from pore adsorption to cake formation in which case, aggregate structure was most significant for flux decline. In nanofiltration, rejection of natural organics involved both size and charge exclusion. Fouling was caused by precipitation of a calcium-organic complex and could be avoided by pre-treatment with metal salt coagulants.

Clay particles such as montmorillonite, kaolinite and bentonite are not suitable for use as adsorbents upstream of a polypropylene microfiltration membrane. Activated carbon, and magnetite are ideal adsorbents in terms of hydraulic resistance. Ball clay and MIEX cause a modest decline in membrane flux, but warrant further study. The potential of the membrane-compatible adsorbents to remove natural organic matter from water, either alone or in combination must be evaluated. The membrane performance of these adsorbents must be revisited in "real" water, where adsorbed organics can change the nature of the filter-cake, and influence particle-membrane interactions. Residual organic matter will also impact on membrane performance in a “real” water system.
6. Coagulation and Microfiltration

6.1 Method

6.1.1 Laboratory evaluation of coagulants for use in MF

The raw water source used was the East Moorabool River near Anakie, Victoria. This water has a relatively high total organic carbon content (8-12mg/L) and relatively low turbidity (3.9 NTU).

The water was treated in standard jar tests with several different coagulants (CSIRO Internal Reports FE-76 and FE-83). The coagulants used were alum (Akzo-Nobel), polyaluminium chloride (Hardiman), polyaluminium chlorohydrate (Orica), ferric chloride, polyferric sulphate (Aluminates), and a 50/50 alum/polyferric sulphate mixture (Aluminates). The water was treated as two lots, collected at different times of the year. The aluminium-based coagulants were tested on one batch of water (Lot#1) and the iron-based coagulants on a separate batch (Lot#2). Both batches of water were treated with alum, to provide a basis for comparison between both water batches and across all coagulants. The jar test procedure was to adjust the pH of one litre of raw water from 7.5 to 6.0 with sulphuric acid. The water was then dosed with coagulant as required. After each chemical addition the water was stirred for 60s at 250RPM. The pH was maintained at 6.0 throughout the procedure with sulphuric acid or sodium hydroxide. Once dosing was complete the mixture was stirred for 90 seconds at 100 RPM.

The treated water was filtered through a 0.45µm filter (Selby-Biolab HPLC-certified) and measured for dissolved organic carbon and ultra-violet absorbance after 30mins settling. Ultra-violet absorbance was measured at 254nm (Shimadzu UV-160 UV-visible spectrophotometer). Dissolved organic carbon was measured by wet chemical oxidation (OI Analytical 1010 Wet Oxidation TOC Analyser).

6.1.2 Pilot plant evaluation of coagulants for use in MF

Different coagulants were used in pilot plant tests as a pre-treatment prior to microfiltration of the water. The same range of coagulants that were evaluated on the laboratory single fibre membrane rig were tested in order to determine whether there were differences in their behaviour in continuous membrane trials. Alum was used as the “benchmark” to which all the other coagulants and pre-treatment regimes were compared. Jar tests were performed at regular intervals to determine the “optimum” alum dose for the raw water to ensure maximum TOC removal. In most cases this resulted in an alum dose to the plant equivalent to 1.4 mg/L (as Al\(^{3+}\)). The pilot plant was designed to flash mix the coagulant in the first contact tank where a Rushton style turbine ensured high levels of turbulent mixing at coagulant dosing point. The second contact tank was similarly mixed and could be dosed with polyelectrolyte or other chemicals at the eye of the impellor. The remaining two contact tanks were fitted with axial flow impellors that gave low levels of shear and ensured good plug flow through the remainder of the flocculation stage. An acid/caustic dosing point in the second contact tank allowed pH to be regulated at the required level throughout the coagulation and flocculation stages.

In these tests, the flocculated raw water was passed directly to the microfiltration unit for membrane filtration, as solids separation in the high rate settler was not effective.

Another trial was performed to determine whether alum floc recycled back to the contact stage would provide a nucleation site for the formation of a better quality floc particle for presentation to the membrane surface. In these experiments, alum floc was settled in the separation stage, recovered and dosed back to the contact stage at the point where alum was being dosed into the plant. The dose of alum into the plant was maintained at a dose equivalent to 1.4 mg/l Al\(^{3+}\). The water containing the alum/floc particles was then dosed directly to the MF membrane.
In the laboratory tests a small dose of polyelectrolyte was added in an attempt to modify the alum floc structure before the MF stage. This was repeated in the pilot plant using an alum dose equivalent to 1.4 mg/L Al$^{3+}$ and 0.2 mg/L of Ciba LT20 (originally Allied Colloids LT20), a neutral high molecular weight polyacrylamide. The alum was dosed into the first mixing tank in the contact stage and the polyelectrolyte into the second mixing tank. Alum/polyelectrolyte flocs were dosed directly to the MF membrane. The membrane performance was compared to another run using alum alone as the pre-treatment at a dose equivalent to 1.4 mg/L Al$^{3+}$.

Figure 11. DOC and UV$_{254}$ removal from Moorabool water treated with selected Fe and Al based coagulants, compared to alum

6.2 Results

6.2.1 Laboratory evaluation of coagulants for use in MF

The UV$_{254}$ and DOC removals from Moorabool water, achieved with the aluminium and iron-based coagulants are shown in Figure 11. For the aluminium-based coagulants, the minimum DOC achieved was approximately 4 mg/L, at a dose of 119 µmol/L. The DOC removals for alum, polyaluminium chloride and polyaluminium chlorohydrate were similar.

The minimum UV$_{254}$ achieved was approximately 0.060 at a dose of 119 µmol/L. The UV$_{254}$ removals for alum and polyaluminium chloride were similar, although the UV$_{254}$ removal for polyaluminium chlorohydrate was significantly lower (0.110 at 148 µmol/L). The elevated
UV$_{254}$ values for polyaluminium chlorohydrate appear to be caused by hydrolysis of residual coagulant, which gave the treated water a cloudy appearance. For the iron-based coagulants, the minimum DOC achieved was approximately 5.5mg/L at a dose of 148µmol/L. The DOC removals for ferric chloride, polyferric sulphate, and the alum/polyferric sulphate mixture were similar. The minimum UV$_{254}$ achieved was approximately 0.100 at a dose of 148µmol/L. The UV$_{254}$ removals for ferric chloride, polyferric sulphate, and the alum/polyferric sulphate mixture were similar. The elevated UV$_{254}$ values at low doses were caused by the UV-absorbance of iron in solution when the concentration was too low for coagulation to occur.

**Figure 12 Microfiltration of Moorabool water treated with Fe and Al based coagulants**

(at doses of 119 and 148µmol/L (as Al$^{3+}$ and Fe$^{3+}$ respectively) and pH 6.0)

The flow rates of microfiltration membrane permeate, as a function of permeate throughput, for Moorabool water, pre-treated by the aluminium and iron-based coagulants are shown in Figure 12. In all cases, the rate of fouling after coagulation pre-treatment was lower than for the raw water. For the aluminium-based coagulants, the rates of fouling were similar. The declines in permeate flow rate after 800g of permeate was filtered were 51%, 52% and 51% for alum, polyaluminium chloride, and polyaluminium chlorohydrate respectively. For the iron-based coagulants, the rates of fouling by ferric chloride and polymerised ferric sulphate were slightly higher than for alum, but the rate for alum/polymerised ferric sulphate was similar to alum. The declines in permeate flow rate after 800g of permeate was filtered were 61%, 62%, 67%, 71% for alum, alum/polyferric sulphate, ferric chloride, and polyferric sulphate respectively.

6.2.2 Pilot plant evaluation of coagulants for use in MF

Pilot plant membrane fouling runs after coagulation pre-treatment are shown in Figure 13. The coagulants were each dosed at 1.4 mg/L as Al$^{3+}$ equivalent as determined from jar tests performed on the raw water. The trans-membrane pressure was plotted as a function of permeate throughput at constant flux. The rates of fouling for different coagulants were determined from the TMP rise rates before the first backwash (at approximately 1000 L of throughput). These fouling rates are given in Table 5, with the feed and permeate water quality. As for the single-fibre runs, the rate of fouling after pre-treatment was substantially lower than the rate for untreated water.

The throughput after alum treatment was approximately 10 times higher than without treatment. All coagulants fouled the membrane at similar rates initially (0.02-0.03 Pa/L), except for FeCl$_3$, which fouled substantially faster (0.07 Pa/L). The rate of fouling increased with throughput in all cases.
The permeate quality was similar for all coagulants except for polyaluminium chlorohydrate, which produced treated raw water with the highest UV absorbance. Permeate UV-absorbance was substantially reduced by coagulation pre-treatment in all cases. The rate of fouling was relatively insensitive to variations in the feed UV-absorbance (NOM content).

Table 5. Initial fouling rates and water quality in pilot plant runs on Maroondah water after treatment with alum, PAC, PAC-AC, FeCl₃, PFS and alum-PFS at pH 6.0.

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>Initial Fouling Rate [Pa/L]</th>
<th>Turbidity [NTU]</th>
<th>UV₂₅₄ [Pa/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed</td>
<td>Permeate</td>
<td>Feed</td>
</tr>
<tr>
<td>Untreated</td>
<td>0.213</td>
<td>0.3</td>
<td>0.083</td>
</tr>
<tr>
<td>Alum</td>
<td>0.022</td>
<td>2.3</td>
<td>0.132</td>
</tr>
<tr>
<td>PAC</td>
<td>0.018</td>
<td>2.2</td>
<td>0.113</td>
</tr>
<tr>
<td>PAC-AC</td>
<td>0.031</td>
<td>2.2</td>
<td>0.202</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>0.069</td>
<td>2.2</td>
<td>0.160</td>
</tr>
<tr>
<td>PFS</td>
<td>0.034</td>
<td>2.6</td>
<td>0.121</td>
</tr>
<tr>
<td>Alum-PFS</td>
<td>0.030</td>
<td>2.5</td>
<td>0.182</td>
</tr>
</tbody>
</table>

Membrane performance in other trials performed using alum coagulation and various floc-conditioning approaches is shown in Figure 14. The trans-membrane pressure was plotted as a function of permeate throughput at constant flux. The membrane performance was compared to that of untreated raw water and that with alum coagulation and direct membrane filtration. Alum dose was 1.4 mg/L as Al³⁺ and contact pH was maintained at 6.0.

Filtration of water that had previously been membrane filtered, collected and stored is shown in Figure 14. The TMP increase was about 20% over the first 1000 litres of filter throughput, whereas for alum treated raw water, the increase was about 50%. This experiment showed that particulate fouling by alum floc was a major contributor to membrane TMP increase, however, there was still a component remaining in the water that contributed about 40% of the membrane fouling, even after the water had been passed through a MF membrane.
Figure 13: Rates of membrane fouling in pilot plant trials on Maroondah water after treatment with alum, polyaluminium chloride (PAC), polyaluminium chlorohydrate (PAC-AC), ferric chloride (FeCl₃), polyferric sulphate (PFS) and alum-PFS at pH 6.0.
An experiment where alum floc structure was conditioned with a high molecular weight neutral polyelectrolyte is shown in Figure 14. As can be seen, the presence of the polyelectrolyte did not impair membrane performance nor did it improve it compared to filtration of alum floc alone.

The use of alum floc recycle as a method of building denser floc for use in membrane filtration is also shown in Figure 14. As can be seen, the membrane performance was not improved by this approach. The membrane performance was similar to that for the use of alum alone.

**6.3 Discussion**

Treatment of Moorabool water by aluminium and iron-based coagulants resulted in DOC removals that were essentially independent of the type of coagulant used. Although the UV\textsubscript{254} removals were dependent on the type of coagulant used in some cases, this could be due to the absorbance of the coagulant itself, or its hydrolysis products.

The rate of fouling by coagulation-treated water was substantially lower than by the raw water. However, the variation in the rates of fouling between the different coagulants tested was quite small. The two pure iron-based coagulants (ferric chloride and polyferric sulphate) had slightly higher rates of fouling than all of the aluminium-based coagulants (including the alum/polyferric sulphate mixture). The rate of fouling by the polymerised aluminium-based coagulants was similar to alum and the rate of fouling by the polymerised iron-based coagulants was similar to ferric chloride. The variation in fouling rate between aluminium and iron based coagulants cannot be attributed to the kinetics of floc formation, as the laboratory tests were performed after long coagulation times and floc formation would have been complete. The variation in performance between the iron and aluminium based coagulants was most likely due to variations in the structure of the flocs and thus the filter cake produced.

The effect of various coagulants on the rate of fouling will depend on the characteristics of the raw water. Moorabool water had low turbidity and a high DOC concentration. Water of a different quality may require different coagulant doses to meet NOM removal requirements, which in turn may alter the relative contributions by residual NOM and flocs.
Industrial experiences indicate that pre-polymerised aluminium-based coagulants may lead to better membrane performance for some waters (Reference 5) as the time between chemical cleans can be extended. Qualitative results from our pilot plant studies confirmed that backwashing the pre-polymerised aluminium-based coagulants was easier than when alum was used. The ease of backwashing may be linked to the time required between chemical cleaning as floc penetration into the membrane pores is more likely if solids are only partially removed from the membrane module during the backwash stage.

The pilot-plant trials confirmed the laboratory results that showed MF fouling rate was independent of the coagulant type. On this basis, it seems likely that the fouling of the 0.2µm polypropylene microfiltration membrane was insensitive to structural differences in the flocs formed from the different coagulants tested. Structural features such as floc permeability and fracture tendency under hydrodynamic shear at the membrane surface may be of secondary importance compared to the size and quantity of the smallest flocs. If this is the case, using a polyelectrolyte with the coagulant may reduce fouling. However, experiments performed to demonstrate whether “bolstering” alum flocs by recycle of flocs from the backwash tank to head of plant or by use of polyelectrolytes indicated that these approaches made no difference to membrane performance. These results indicate that it is probably not the cake resistance of the floc layer or the size and quantity of small flocs that are the major inhibitory factors limiting membrane flux. Rather it is the residual organics remaining in the water after coagulation that are inhibiting membrane performance.

There appeared to be no benefit from using any of the pre-polymerised metal coagulants, compared to using alum alone, apart from marginally improved backwashing of solids off the membrane. As mentioned earlier, the benefits of improved solids removal during backwashing may be reflected in longer operating times between chemical cleaning. Longer-term trials using alum compared to the pre-polymerised coagulants would be required to quantify this benefit.

6.4 Conclusions

The rate of fouling of a polypropylene microfiltration membrane by Moorabool water was considerably reduced when the water was pre-treated by coagulation compared to the filtration of untreated water. The rate of fouling was relatively insensitive to the type of coagulant used. The various commercially available aluminium-based and iron-based coagulants investigated did not reduce the rate of fouling below the rate achieved with alum. However prospects for reducing fouling rates with alternative coagulants may depend upon the characteristics of the raw water, and upon the dose of coagulant required to affect the desired level of treatment.

A variety of traditional and pre-polymerised aluminium and iron-based coagulants were tested for suitability as a pre-treatment for drinking-water microfiltration. All coagulants reduced the rate of fouling, although differences in membrane performance between coagulants were minimal. Floc structure, and kinetic effects appeared to play a secondary role compared to floc size or residual NOM in the fouling of polypropylene microfiltration membranes by the surface waters studied.
7. Hybrid Microfiltration Systems

A range of hybrid systems were performed to evaluate coagulation in combination with NOM adsorption or floc attachment to solid particles, these included:

- Magnetite/alum
- Haematite/ferric sulphate
- MIEX/alum
- Powdered activated carbon/alum

In all cases these systems were fully evaluated in the laboratory in jar tests followed by membrane filtration through the single fibre, microfiltration test rig (CSIRO Internal Reports FE-72, FE-76 and FE-77).

7.1 Method

7.1.1 Laboratory tests

**Magnetite/alum hybrid system**

In these laboratory single fibre membrane tests (CSIRO Internal Report FE-76), magnetite was used with alum coagulation to separate NOM and to attach the alum floc to the surface of the magnetite particles. The magnetite used in these tests was the SIROFLOC grade magnetite with a mean particle diameter of 23 µm and a size distribution as shown in Figure 8b.

The water was treated in standard jar tests with various combinations of magnetite, alum, and LT-20 (Ciba Chemicals) polyelectrolyte (a high molecular-weight, neutral polyacrylamide). The jar test procedure was to adjust the pH of one litre of raw water from 7.5 to 6.0 with sulphuric acid. The water was then dosed with magnetite, alum, and polyelectrolyte as required. After each chemical addition the water was stirred for 60 seconds at 250 RPM. The pH was maintained at 6.0 throughout the procedure with sulphuric acid or sodium hydroxide. Once dosing was complete the mixture was stirred for 90 seconds at 100 RPM.

The treated water was measured for dissolved organic carbon, ultra-violet absorbance and true colour, after 30 minutes settling. All samples for water quality were filtered through a 0.45 µm filter (Selby-Biolab HPLC-certified) prior to analysis.

In combined magnetite-alum treatment cases, the extent of magnetite-alum attachment was measured from the residual aluminium content in the treated water after the jar contents were allowed to settle for 150 seconds.

Membrane performance tests of various treatment options were performed on the CSIRO built single hollow-fibre rig described previously. The membrane feed water was prepared using the jar test procedure described above, although 1.5 litre batches of water were used, and the 100 RPM stirring regime was omitted. The feed suspension was stirred at 250 RPM and the pH was controlled at 6.0 (Prominent pump and controller) throughout the membrane performance test. In some cases, the feed suspension was allowed to settle, and only the supernatant was pumped onto the membrane. The membrane feed pressure and permeate throughput (A&D 6000FG balance) were logged with data acquisition software (Genie), and the permeate flow rate was calculated from the differential throughput.

**Haematite/ferric sulphate hybrid system**

The haematite ferric sulphate hybrid system was based on the use of a "waste" product from the manufacture of ferric sulphate coagulant. Aluminates Ltd make a grade of ferric sulphate at their Moe, Victoria plant, by dissolving haematite in sulphuric acid. The residual from that process is a sludge that contains fine haematite particles (between 1 and 10 µm diameter) in a solution of ferric sulphate that is normally disposed of through filter presses.
and land-fill. We were keen to determine whether this waste stream could be utilised as a basis for a hybrid membrane system.

The ferric sulphate content of the slurry was determined by ICP analysis and was used as the basis for dosing it into the raw water. The correct dose of ferric sulphate was determined by jar tests on the raw water and used to calculate the dose of the ferric sulphate/haematite slurry needed in the single fibre membrane tests.

A couple of exploratory hybrid membrane trials were performed in the laboratory to determine whether the haematite particles would cause major problems on the MF membrane. As this was not the case, the haematite/ferric system was evaluated in greater depth at the pilot plant scale.

**MIEX/alum hybrid system**

MIEX resin was evaluated as an adsorbent for NOM from East Moorabool water (CSIRO Internal Report FE-77) in jar tests. The MIEX resin was used before, during or after alum coagulation of the water and the resultant water passed through the single fibre membrane test rig to determine rates of membrane fouling.

The MIEX resin used in these experiments was obtained from the CSIRO Molecular Science group that were manufacturing large-scale batches of resin for ORICA. A half litre sample of the washed resin from the manufacturing process was taken to the laboratory where it was re-washed. This was achieved by mixing, settling and decanting the resin in a two-litre glass beaker, with deionised water. Once a clear supernatant was obtained (turbidity less than 1 NTU) the resin was washed a further three times using MilliQ water.

The effects of resin dose, contact time and pre-, post- or simultaneous treatment of the water with alum coagulation were assessed. In the kinetic tests, removal rates of $\text{UV}_{254}$ absorbance, from the water, were used to determine the response to coagulation conditions and MIEX dose. MIEX doses in the range 0.1 to 3.6 g/L (on a dry solids basis) were used in these tests.

**Powdered activated carbon/alum hybrid system**

Cunli Xiang (RMIT) used a similar approach to study the use of activated carbon as an adsorbent for NOM before microfiltration (Publication 16). In these experiments, the powdered activated carbon used was a highly meso-porous water treatment grade of powdered activated carbon from Char International. The activated carbon had a mean particle diameter of 39 $\mu$m and contained 25% ash. The carbon adsorption step was applied either after alum coagulation or simultaneously with the coagulation step. In some tests, the carbon was separated before the membrane (either by settling or filtration through Watman GF/A filter paper) and in other tests it was fed directly to the membrane with the associated alum floc. Other tests were performed where a pre-coat of the carbon was formed on the membrane surface prior to the filtration of the alum treated water through the membrane.

**7.1.2 Pilot Plant trials**

The hybrid systems with the best performance, determined from the single fibre laboratory tests were evaluated in pilot plant trials. This meant that the following hybrid systems were tested (Publications 1 and 5 and CSIRO Internal Report FE-83):

- Magnetite/alum
- Haematite/ferric sulphate
- Powdered activated carbon/alum

**Magnetite/alum hybrid system**

Two grades of magnetite were used in these trials, the coarser SIROFLOC grade and a finer magnetite grade from Tiwest Ltd. in WA.

The SIROFLOC grade magnetite (23 $\mu$m mean particle diameter and size distribution as shown in Fig. 2b) was used continuously, dosed into the second contact tank, after alum addition. The pH of the contact stage was controlled at 6.0 by the addition of sulphuric acid.
into contact tank one. The magnetite doses assessed in the pilot plant trials were 0.1 g/L, 1.0 g/L and 10 g/L. The magnetite/alum hybrid system was investigated using two different approaches, either fed directly to the membrane with the associated alum flocs or separated in the high rate settler and then fed to the membrane. In both cases the magnetite was recovered (from the settler and membrane backwash), regenerated using NaOH at pH 11, washed with raw water once on a magnetic drum separator and reused. The finer Tiwest magnetite (equivalent in size to the pigment grade magnetite shown in Fig. 2b) was used as a slurry, and dosed at 0.1 g/L into the contact stage on a used once basis. It was then collected from the MF backwash and the solids separator and stored before it was regenerated and washed batch-wise using NaOH at pH 11 and raw water, respectively.

Haematite/ferric sulphate hybrid system

The haematite ferric sulphate hybrid system was based on the use of the Aluminates “waste” product from the manufacture of ferric sulphate coagulant, as described in the laboratory single fibre membrane tests. The ferric sulphate content of the slurry was determined by ICP analysis and was used as the basis for dosing it into the raw water. The haematite/ferric slurry was dosed using the raw water UV\textsubscript{254} absorbance as a guide. The dose was set to give the same treated water UV\textsubscript{254} absorbance as the previous day’s control run using alum coagulation. The correct dose of ferric sulphate was determined by jar tests on the raw water and used to calculate the dose of the ferric sulphate/haematite slurry needed in the pilot plant.

The slurry was dosed into the contact stage with the associated haematite particles acting as a surface for attachment of the ferric hydroxide flocs, similar to the magnetite/alum hybrid system. The haematite dose to the plant, under these conditions, was about 2.8 mg/L. The pH in the contact tanks was controlled to 5.5 by the addition of sulphuric acid into the first contact tank. In other experiments, the slurry was dosed into the water with no pH control, in which case the pH was generally around 6.0 in the contact stage.

There was no attempt made to recover the haematite particles for reuse and they were disposed of with their associated ferric hydroxide floc.

Powdered activated carbon/alum hybrid system

The powdered activated carbon trials were performed using a highly meso-porous water treatment grade of powdered carbon from Char International. The carbon particle size was sub-45 µm and it contained 25% ash. The carbon was used in two different ways. The first was as a body feed where the carbon was dosed continuously into the second contact tank (after alum dosing) and then passed straight to the membrane. The second approach was to pre-coat the membrane with the carbon before the alum treated water was fed to the membrane. In the second case, the amount of carbon pre-coated onto the membrane was approximately 200 g, equivalent to the amount that would have been dosed over the trial period if it had been dosed at 40 mg/L. In all cases, the raw water was alum treated beforehand using an alum dose equivalent to 1.4 mg/L Al\textsuperscript{3+} at a pH controlled to 6.0 using sulphuric acid dosed to contact tank one.

7.2 Results

7.2.1 Laboratory tests

MIEX/alum hybrid system

Despite the rigorous washing of the MIEX resin used in these tests, there appeared to be fine iron oxide particles present in the treated water from jar tests. These iron oxide fines were observed to foul the microfiltration membrane rapidly and so the solutions were filtered through Watman GF/C grade filter papers before the membrane separation stage.
Table 6: Combined alum coagulation and MIEX resin adsorption UV$_{254}$ and TOC results

<table>
<thead>
<tr>
<th>Test</th>
<th>UV Absorbance @ 254 nm Before MF</th>
<th>TOC (mg/l) Before MF</th>
<th>Test</th>
<th>UV Absorbance @ 254 nm After MF</th>
<th>TOC (mg/l) After MF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.148</td>
<td>6.53</td>
<td>1</td>
<td>MIEX adsorption then GF/C filtered</td>
<td>0.036</td>
</tr>
<tr>
<td>1</td>
<td>Alum coagulation then GF/C filtered</td>
<td>0.057</td>
<td>2</td>
<td>Alum coagulation then MIEX adsorption then GF/C filtered</td>
<td>0.017</td>
</tr>
<tr>
<td>2</td>
<td>MIEX adsorption then GF/C filtered</td>
<td>0.036</td>
<td>3</td>
<td>Simultaneous alum coagulation and MIEX adsorption then GF/C filtered</td>
<td>0.028</td>
</tr>
</tbody>
</table>

The TOC and UV$_{254}$ removals from Moorabool water by adsorption onto MIEX resin either alone or in combination with alum coagulation are shown in Table 6 before and after filtration through the polypropylene microfiltration membrane. The kinetics and equilibrium experiments indicated that the best MIEX dose to use was 1.0 g/L (as dry resin) with a contact time of 10 minutes (achieved > 80% of equilibrium capacity in 10 minutes).

The membrane performance is shown in Figure 15 and summarised in Table 7 as throughput to a limiting membrane flux of 8 g/minute for each of the water pre-treatment regimes tested. The limiting membrane flux was normalised by dividing the flux by the raw water flux.

Table 7 Membrane throughput to limiting flux of 8 g/minute for various alum/resin pre-treatment regimes

<table>
<thead>
<tr>
<th>Jar Test</th>
<th>Conditions</th>
<th>Throughput to 8 g/min (g)</th>
<th>Normalised throughput</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw water</td>
<td>30</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Alum coagulated only</td>
<td>56</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Resin treated GA55 filtered</td>
<td>34</td>
<td>1.1</td>
</tr>
<tr>
<td>2</td>
<td>Alum then resin GA55 filtered</td>
<td>515</td>
<td>17.2</td>
</tr>
<tr>
<td>3</td>
<td>Alum and resin GA55 filtered</td>
<td>357</td>
<td>11.9</td>
</tr>
</tbody>
</table>

Figure 15. Microfiltration performance of Moorabool water pre-treated by coagulation and MIEX resin adsorption
Magnetite/alum hybrid system

The dissolved organic carbon, ultra-violet absorbance and true colour of Moorabool water treated with various doses of magnetite are shown in Figure 16(a), (b) and (c) respectively. Relatively high magnetite doses (several grams per litre) were required for NOM removal, because of magnetite’s relatively low surface area (2-3cm$^3$/g). At a dose of 10g/L, the removal of DOC, UV$_{254}$, and colour, were approximately 19%, 31%, and 36% respectively. At magnetite doses below 1g/L the DOC removal was negligible.

![Figure 16: DOC, UV$_{254}$ & colour removal from Moorabool water versus magnetite dose](image)

The optimum alum dose (at 0g/L magnetite) for NOM removal was approximately 3.2mg/L as Al$^{3+}$. At this dose, the removal of DOC, UV$_{254}$, and colour, were approximately 44%, 64%, and 92% respectively. The combined magnetite-alum treatment resulted in improved DOC and UV$_{254}$ removal over alum alone, at alum doses below the optimum 3.2mg/L and magnetite doses of 1g/L or higher. However, the change in water quality decreased as the alum dose increased.
When alum and magnetite treatments were combined, attachment of alum flocs onto magnetite occurred at relatively low magnetite doses, as shown in Figure 17(d). At an alum dose of 3.2mg/L (as Al\textsuperscript{3+}), a magnetite dose of 0.01g/L was sufficient to attach 34% of the alum flocs formed (as Al\textsuperscript{3+}). At the optimum alum dose, and magnetite doses of 0.1g/L, and above, the concentration of unattached alum flocs (as Al\textsuperscript{3+}) dropped below the aluminium concentration of the raw water.

The membrane filtration performance of the magnetite/alum treated water is shown in the Figure 17: Water quality after alum/magnetite treatment of Moorabool water (Magnetite doses of 0, 0.1, 1.0 and 10 g/L).

Figure 18(a). The decline in permeate flow rate is shown as a function of throughput after treatment with various doses of magnetite followed by 3.2mg/L of alum (as Al\textsuperscript{3+}) at pH=6.0. The dashed curves represent performance when the magnetite/alum particles were allowed to settle before microfiltration. The permeate throughput at which the permeate flow rate dropped to 7.0g/min (approximately 25% of the initial flow rate) is shown in Figure 18(b). The dissolved organic carbon, ultra-violet absorbance, and true colour of alum-treated East-Moorabool water before and after membrane treatment are given in Table 2.
From Figure 18(b) it can be seen that there was no improvement in membrane performance for magnetite/alum treatment compared to alum alone, when the magnetite dose was below 0.1g/L. However, at a dose of 1.0g/L, the throughput was 2.5 times greater than for alum alone, and at a dose of 10g/L, 4 times greater. In all cases, settling of the magnetite-alum particles, followed by microfiltration of the treated water did not improve membrane performance.

The membrane performance was also investigated when a polyelectrolyte was added in addition to alum and magnetite. A polyelectrolyte may become necessary in full-scale processes to reduce magnetite-alum detachment and break-up under ubiquitous shear forces. The rate of fouling was unaffected at polyelectrolyte doses below 0.6mg/L but increased at higher doses. There was no improvement in the rate of fouling over alum alone for hybrid treatments with doses of magnetite up to 0.1g/L. However, at a magnetite dose of 1g/L, a 3-fold increase in throughput was achieved, and at a magnetite dose of 10g/L, a 4.5-fold increase in throughput was possible.

**Haematite/ferric sulphate hybrid system**

There was minimal laboratory testing of the haematite/ferric sulphate system apart from analysis to determine the iron concentration, jar tests to determine what dose was required for effective TOC and UV$_{254}$ removal and exploratory single fibre membrane filtration tests. The jar tests showed that a dose of 38 mg/L of the haematite/ferric slurry was required for optimal removal of TOC and UV$_{254}$ absorbance, this was equivalent to a ferric dose of 2.1 mg/L as Fe$^{3+}$. The laboratory tests confirmed that the haematite particles had no detrimental impact on the MF performance when dosed into MilliQ water at the above dose rate.

**Powdered activated carbon/alum hybrid system**

A similar study (Publication 16) was done for the treatment of Moorabool water using powdered activated carbon with and without alum coagulation. Table 8 shows the TOC and UV$_{254}$ absorbance results from these tests.

The membrane filtration performance on Moorabool water treated using coagulation and powdered activated carbon adsorption is shown in Figure 19, compared to the filtration of MilliQ water and raw water.
Table 8: Water quality after pre-treatment of East Moorabool water with powdered activated carbon/alum hybrid system

<table>
<thead>
<tr>
<th>Test</th>
<th>Pre-treatment method</th>
<th>TOC (mg/L)</th>
<th>UV Absorbance @ 254 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw water</td>
<td></td>
<td>8.2</td>
<td>0.23</td>
</tr>
<tr>
<td>0.45 µm filtered raw water</td>
<td></td>
<td>8.1</td>
<td>0.18</td>
</tr>
<tr>
<td>1</td>
<td>3.2 mg/L Al coagulation, filtered by 0.45 µm membrane</td>
<td>5.1</td>
<td>0.075</td>
</tr>
<tr>
<td>2</td>
<td>100 mg/L PAC adsorption for 70 hours then filtered by GF/A filter</td>
<td>2.9</td>
<td>0.075</td>
</tr>
<tr>
<td>3</td>
<td>3.2 mg/L Al coagulation, filtered by GF/A filter, then 100 mg/L PAC adsorption for 70 hours, filtered by GF/A filter</td>
<td>1.4</td>
<td>0.007</td>
</tr>
<tr>
<td>4</td>
<td>3.2 mg/L Al coagulation, filtered by GF/A filter, then 10 mg/L PAC adsorption for 30 minutes, filtered by GF/A filter</td>
<td>3.5</td>
<td>0.045</td>
</tr>
</tbody>
</table>

7.2.2 Pilot Plant trials

The MF performance of the three main hybrid systems, tested on the pilot plant, is summarised in Figure 20, in comparison to direct membrane filtration of alum coagulated raw water.

Magnetite/alum hybrid system

There were extensive trials performed on the magnetite/alum hybrid system as this system was felt to have the most potential for improved membrane performance.

The effect of magnetite dose, when using the SIROFLOC™ grade of magnetite, demonstrated quickly that a dose of at least 1 g/L of magnetite was required to see improved membrane performance. A trial performed at a magnetite dose of 0.1 g/L, confirming previous laboratory results, showed the rate of TMP development to be the same as that for alum alone. There was no benefit seen from running at the highest magnetite dose of 10 g/L and as a result a magnetite dose of 1 g/L was used in all subsequent trials. Unfortunately, this dose was not low enough to enable magnetite to be used on a once through basis and required it to be collected, regenerated and reused. A magnetite dose of 1 g/L did mean that the size of the magnetite storage and regeneration system could be much smaller as would the dose of NaOH required for regeneration of the magnetite. Figure 20 shows the typical membrane performance under a treatment regime...
where magnetite was dosed continuously at 1 g/L into the contact stage with an alum dose of 1.4 mg/L Al$^{3+}$.

Pilot plant trials using the finer Tiwest grade of magnetite were performed at a dose of 0.1 g/L. These trials gave a worse membrane performance than alum alone as the membrane pre-treatment. As a result the use of this magnetite was abandoned.

![Figure 20: Pilot plant membrane performance with hybrid coagulant/particle pre-treatment systems](image)

**Haematite/ferric sulphate hybrid system**

Figure 20 shows the performance of the haematite/ferric system at a slurry dose of 38 mg/L, equivalent to a ferric dose of 2.1 mg/L as Fe$^{3+}$ and a haematite dose of 2.8 mg/L. Under this dosing regime, the membrane performance was similar to that of the magnetite/alum system. Backwash TMP recovery was good as particle separation from the membrane module was effective.

In another set of trials using the haematite/ferric system where the dose of haematite was about 10 times higher (about 30 mg/L) than that shown in Figure 15, the rate of TMP development was much greater and limited the trial to a very short run. This indicates that the dose of haematite particles used is critical and should be limited to around 2 to 3 mg/L.

**Powdered activated carbon/alum hybrid system**

The use of powdered activated carbon and alum as a pre-treatment before the MF was assessed in the pilot plant with the carbon used as either a pre-coat on the membrane or as body-feed into the coagulated water before the membrane filtration stage.

When used as body-feed at a dose of 40 mg/L of carbon and an alum dose of 1.4 mg/L as Al$^{3+}$, the membrane performance was only marginally improved, as shown in Figure 20. In these trials, the estimated contact time for the carbon and water, before the membrane filtration step was between 3 and 5 minutes. The UV$_{254}$ absorption of the treated water was reduced by about 30 %, compared to alum treated water alone. The use of carbon in this way resulted in rapid rises in TMP across the membrane; however, TMP (and flux) recovery after backwashing was extremely effective.

When the carbon was used as a pre-coat, the performance of the membrane on alum-coagulated water was no different to that of alum treated water fed to an uncoated membrane. In this configuration, the contact time between the carbon and water at the
membrane surface was negligible. There was an insignificant difference between the UV$_{254}$ absorbance of the filtered water from the pre-coated membrane and a non-coated membrane. Again, there was good TMP recovery on backwash with this system of powdered activated carbon use.

7.3 Discussion

7.3.1 Laboratory tests

MIEX/alum hybrid system

Just dosing resin into the raw water removed about 50% of the TOC and 75% of UV$_{254}$ organics, in the absence of alum coagulation. MIEX resin pre-treatment by itself was ineffective at improving membrane performance and gave similar membrane performance to the filtration of raw water and worse performance than filtration of the alum coagulated water.

The pre-treatment of raw water by alum coagulation followed by floc separation and then adsorption using MIEX® resin was demonstrated to improve microfiltration membrane performance. This pre-treatment regime effectively reduced TOC in the water by 74%. The membrane performance was significantly improved, with over 15 times the water throughput being achieved before the flux had declined to 85% of the starting flux, when compared to filtration of raw water.

When the resin and alum were added simultaneously, NOM removal was reduced slightly as shown by the 65% reduction in TOC. Membrane performance was slightly inferior to that achieved by the sequential alum/resin treatment process. The membrane throughput before the flux declined to 85% of the starting flux was over 10 times more than when filtering raw water.

Based on these tests there appeared to be a correlation between residual TOC in the resin treated water and membrane breakthrough flux, as shown in Graph 21.

The dose of MIEX® used in the laboratory experiments was quite high and, from a process economics perspective, it would mean that the resin would need to be recovered, regenerated and reused. The experiments indicate that there is significant potential to
improve the microfiltration membrane performance of raw water if adsorption of organics is carried out in combination with alum coagulation. From a process simplicity perspective it would be preferable if the resin and alum could be added simultaneously.

It is clear from these tests that the alum coagulated and filtered water contains some species that cause fouling of the microfiltration membrane. It is unclear whether these are micro-floc that have not been swept up into the larger alum floc or organic molecules that are not removed by the alum coagulation process. In any case the use of the MIEX® resin during or after the coagulation stage effectively separates a proportion of these species and allows for improved microfiltration membrane throughput before backwashing. Classically it is assumed that alum coagulation removes the higher molecular weight charged and possibly some of the hydrophobic organics from the water. The MIEX® resin is thought to be effective at adsorbing the lower molecular weight charged organics from water, so, in this way, it could be that the combined alum and resin approach provides a complimentary removal of organics from the water. However, it is assumed that the types of organics that interact with the membrane surface will be the hydrophobic fractions, and for pore blockage it would tend to be the high molecular weight fraction. It is possible that the MIEX® resin performs two roles in combination with alum, the first to nucleate the flocculation of destabilised colloids, leading to a more effective separation of the alum flocs and secondly to adsorb the charged low molecular weight fractions.

**Magnetite/alum hybrid system**

Microfiltration removed 11% of the dissolved organic carbon content of the natural organic matter present in East Moorabool River water. However, the permeate flow rate declined rapidly during filtration. The flow rate dropped to 75% of the initial value after only 35g of water was filtered.

When the East Moorabool River water was treated with 3.2mg/L of alum (as Al^{3+}), before microfiltration, the DOC removal increased to 44%. During filtration, the permeate flow rate dropped by 25% after 110g of water was treated. Alum treatment before microfiltration gave considerably better membrane performance and water quality than microfiltration alone. The benefit from incorporation of NOM into alum flocs outweighed the impact of the higher membrane solids loading.

When alum at pH=6.0 was added into a water previously dosed with magnetite, flocculation occurred primarily onto the magnetite, leaving few unattached alum flocs. These magnetite-alum particles were retained by the microfiltration membrane and resulted in a lower resistance to filtration than alum flocs alone, thereby improving filtration performance. At magnetite doses below 1.0 g/L, there was no improvement in water quality over alum alone, although at a magnetite dose of 10 g/L, the DOC removal increased slightly to approximately 49 % (from 44 %). The membrane filtration performance of magnetite-alum treated water was substantially better than the filtration performance of water treated only with alum. Magnetite doses of 1.0 g/L and 10 g/L gave throughputs of 270 g and 460 g respectively, before the permeate flow rate dropped to 75 % of the initial value, a substantial improvement (throughputs were 2.5 and 4 times higher respectively) over performance with alum alone. The improvement in membrane filtration performance of this combined magnetite/alum treatment was felt to warrant further study of this system at pilot scale.

Although membrane filtration performance was improved by a combined magnetite/alum treatment, there was still a substantial decline in permeate flow rate with throughput in these systems. Two possible contributions to this decline were residual NOM, which was not removed by chemical treatment, but was partially removed by subsequent microfiltration, and the particles and flocs generated in the course of treatment, which offer a resistance to filtration when retained by the membrane. To distinguish between these two contributions, in some cases the magnetite/alum treated water was allowed to settle before microfiltration. However, there was no improvement in performance observed when compared to experiments where the treated water was stirred continuously during filtration. This was true at magnetite doses of 0 g/L, 1.0 g/L and 10 g/L. In these cases, the decline in
membrane filtration performance must be due to suspended or dissolved material remaining in the treated water after coagulation and sedimentation. This material could be untreated NOM, unattached alum pin flocks or some other component in the raw water. In all cases, microfiltration removed some dissolved organic carbon and ultraviolet absorbance even after alum or magnetite/alum treatment. However, the difference between DOC and UV$_{254}$ absorption before and after the membrane were always too small to allow correlation with membrane performance. If fouling were caused by small-unattached alum pin flocs, then the concentration of aluminium from which these flocs are constituted would be less than 0.5 mg/L, after the magnetite/alum treatment. This aluminium concentration is lower than the aluminium concentration in the raw water. Further work is necessary to understand the causes of fouling in the magnetite/alum-microfiltration treatment process.

Polyelectrolytes are routinely added to water as a flocculant aid. Shear forces that tend to damage flocs, and destabilize magnetite/alum particles will be more significant in pilot-scale microfiltration than in laboratory-scale microfiltration. However, including a polyelectrolyte in the magnetite/alum system should produce a more robust particle. A polyelectrolyte dose of 0.2 mg/L of LT-20 (a high molecular weight, neutral polyacrylamide) was added to the magnetite/alum system, without any adverse impact on membrane performance. The improvement in membrane performance achieved by adding 1.0 g/L and 10 g/L of magnetite before alum and polyelectrolyte treatment was comparable to the improvement in the absence of polyelectrolyte. This indicated that either the polyelectrolyte dose was insufficient to assist pin floc attachment or there was another component remaining in the water that was causing the loss of membrane performance.

Haematite/ferric sulphate hybrid system

There was minimal laboratory testing of the haematite/ferric sulphate system apart from analysis to determine the iron concentration, jar tests to determine what dose was required for effective TOC and UV$_{254}$ removal and exploratory single fibre membrane filtration tests.

Powdered activated carbon/alum hybrid system

Although the removal of UV$_{254}$ by alum coagulation (at a dose of 3.2 mg/L Al$^{3+}$) was similar to that removed by powdered activated carbon adsorption (at a carbon dose of 100 mg/L and contact time of 24 hours), the removal of TOC and UV$_{400}$ were very different. NOM contributing to colour (as determined by UV$_{400}$ absorbance) was easily removed by alum coagulation, however, this portion of the NOM was not effectively removed by carbon adsorption, suggesting the fraction of NOM removed by alum and by carbon were different. Combining alum coagulation (at a dose of 3.2 mg/L Al$^{3+}$) and powdered activated carbon adsorption (at a carbon dose of 100 mg/L and contact time of 24 hours) removed most of the organics. Decreasing the carbon dose to 10 mg/L and the adsorption time to 30 minutes still led to the removal of more than 93 % of UV$_{400}$, 80 % of UV$_{254}$ and 57 % of the TOC.

The MF performance on East Moorabool water pre-treated using the powdered activated carbon/alum hybrid system is summarised in Table 9. The improved membrane performance under these treatment regimes seems impressive. However, the dose of activated carbon and the contact times needed to achieve this level of performance would be unrealistic in practice. The activated carbon dose would need to be kept between 10 and 40 mg/L for the process to be economically viable if the carbon is not recovered and reused. A carbon adsorption time of 30 minutes is still quite a long time in practice and would represent a significant capital cost on a full-scale plant. The laboratory tests at carbon doses and adsorption times within this order of magnitude demonstrated that enhanced membrane throughput was possible.
Table 9 Summary of laboratory performance of powdered activated carbon/alum hybrid treatment system on East Moorabool water.

<table>
<thead>
<tr>
<th>Treatment Process</th>
<th>TOC removal</th>
<th>Relative Membrane Throughput (At 80 % of original flux)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MF only</td>
<td>1.2 %</td>
<td>1</td>
</tr>
<tr>
<td>PAC + GF/A + MF (PAC dose = 100mg/L, 70 hours adsorption time)</td>
<td>65 %</td>
<td>1</td>
</tr>
<tr>
<td>Alum + GF/A + MF</td>
<td>38 %</td>
<td>4</td>
</tr>
<tr>
<td>Alum + PAC + GF/A + MF (PAC dose = 10 mg/L, 30 minutes adsorption time)</td>
<td>57 %</td>
<td>9</td>
</tr>
<tr>
<td>Alum + PAC + GF/A + MF (PAC dose = 100 mg/L, 70 hours adsorption time)</td>
<td>83 %</td>
<td>40</td>
</tr>
</tbody>
</table>

In this Table, MF refers to microfiltration, PAC refers to powdered activated carbon and GF/A refers to filtration through Watman GF/A grade filter paper.

The laboratory tests used filtration through Watman GF/A grade filter paper to separate alum floc and activated carbon particles prior to the membrane filtration step. The use of this filtration step in practice would obviate the need for membrane filtration and so it was eliminated in the pilot plant tests. The laboratory tests did not elucidate whether the carbon particles were capable of capturing and retaining alum floc onto their surface. This would be required if the process is to be a successful pre-treatment system before microfiltration.

7.3.2 Pilot Plant trials

The results shown in Figure 20 indicate that both the magnetite/alum and haematite/ferric hybrid systems foul more slowly than when alum was used alone as the pre-treatment before MF. The differences between Figures 14 and 20 in the performance of the MF system under alum coagulation are as a result of different raw water qualities throughout the year.

**Magnetite/alum hybrid system**

The pilot plant membrane performance, using the magnetite/alum hybrid system, was not improved to as great an extent as it was in the laboratory trials. This was most likely due to higher localised velocity gradients in the pilot plant causing increased shear on the magnetite particles. Visually, there did appear to be free floc present in the membrane feed tank, confirming that floc attachment was a problem.

The most robust hybrid system that utilised magnetite and alum in combination was where the magnetite dose was greater than 1 g/L, allowing for sufficient surface area for floc attachment to the magnetite surface. This system proved to give repeatable performance under conditions where the magnetite had been recycled through many service cycles. However, the process complexity required for this system would increase the capital cost of the membrane process considerably and may also impact on operating costs. Section 8.3.2 discusses this issue in more detail. It is unclear why a membrane filtration step would be needed after this level of treatment; sand filtration of water that has been treated by the SIROFLOC™ process is common practice and results in high quality treated water.

The use of the finer Tiwest grade of magnetite, with its higher surface area, did not enhance membrane performance at lower magnetite doses. The attachment of alum floc to this magnetite was problematic and it was suspected that this material had different surface properties to the SIROFLOC™ grade magnetite. Further work is required to determine the differences between these magnetites to identify why there was a difference between their performance. Another possible reason for the Tiwest magnetite’s failure was that there might have been a large proportion of fine magnetite present in the sample used. Particle sizes of less than a micron would be expected to cause a rapid increase in membrane fouling due to pore blockage.
Haematite/ferric sulphate hybrid system

The similar membrane performance of the magnetite/alum and haematite/alum systems suggests that the “complexity” of the magnetite/alum system could be avoided by dosing of the haematite/ferric slurry directly into the raw water. As this slurry is a by-product from the manufacture of ferric sulphate, it presumably will be a cheap treatment chemical for use in microfiltration.

Further work is required to determine what other materials (eg ferrous ions) are present in this product and whether they would limit its use in drinking water treatment.

Powdered activated carbon/alum hybrid system

The difference between the pilot plant and the laboratory performance using the powdered activated carbon/alum system was probably due to either the lower contact times that were achieved in the pilot plant tests or due to shear effects stripping alum floc from the surface of the carbon particles.

The adsorption of NOM by the carbon was influenced greatly in the pilot plant trials by the contact time that was available before membrane filtration. In the laboratory tests, a contact time of 30 minutes at a carbon dose of 10 mg/L reduced the UV$_{254}$ absorbance by 80% whereas in the pilot plant, contact time was less than 5 minutes and, even with a carbon dose of 40 mg/L, the UV$_{254}$ absorbance was reduced by only 30%. Increasing the contact time before the membrane filtration step to 30 minutes was felt to be impractical in a full-scale system and so it was not attempted on the pilot plant.

The rapid rise in TMP and massive flux recovery on backwash, shown in the case of the powdered activated carbon/alum system, indicates that particulate fouling under this hybrid system was a dominant cause of flux decline. A similar pattern of rapid TMP increase and large flux recovery was not so evident in either the magnetite/alum or the haematite/ferric systems, indicating that particulate deposits on the membrane were not a significant cause of fouling in these approaches. The cause of the particulate fouling in the case of the powdered activated carbon/alum system is most likely due to alum floc detachment from the carbon surface than from the carbon particles themselves. Trials on the pilot plant with carbon dosed into “pure” water (R/O filtered) did not show the same rapid increase in membrane flux as was seen when alum was dosed into the raw water stream.

7.4 Conclusions

Laboratory tests on the magnetite/alum, haematite/ferric sulphate and powdered activated carbon/alum hybrid systems indicated that each of these processes would have potential as a pre-treatment for microfiltration of drinking water. Although the laboratory tests on the powdered activated carbon/alum system showed the greatest potential for membrane throughput enhancement, in practice it was limited by the high contact times required to achieve this level of performance improvement. Overall both the magnetite/alum and haematite/ferric systems gave good increases in MF throughput under reasonable operating conditions.

These laboratory results were confirmed in the pilot plant trials except that the enhancement to membrane throughput was not as great as was demonstrated in the laboratory tests. The powdered activated carbon/alum system, although removing more NOM from the water than the other hybrid systems had a lower level of flux improvement in the pilot plant.

The laboratory and pilot plant trials confirmed that alum floc could be attached to a hard particle and presented to the microfiltration membrane and thus protect it from fouling by the alum floc. The impact of shear in the pilot plant led to a degree of floc separation from the hard particle surface resulting in a reduction in the level of membrane protection that could be achieved. The best improvement in membrane throughput achieved was about twice that achieved with direct dosing of alum into the membrane feed.
The most promising systems that were evaluated in the pilot plant trials were the magnetite/alum and haematite/ferric systems. However, the increased process complexity inherent in the magnetite/alum system would be expected to reduce its economic feasibility. The haematite/ferric system gave the best compromise between process simplicity and improved membrane performance and warrants further study in longer term performance trials.

Although these hybrid approaches eliminated or minimised the effects of particulate membrane fouling, the organics remaining in the water after pre-treatment still resulted in significant fouling of the membrane surface. The fouling mechanism of these residual organics was not fully understood but was most likely due to adsorption of a fraction of these organics within the membrane pore structure. Further work is required to determine whether a suitable adsorbent material can be identified to remove the specific fouling fraction from the residual organics and to combine that adsorbent into a hybrid pre-treatment system. Alternatively a method for modifying the membrane surface to minimise the fouling effects of the residual organics should be developed. This should then be combined with the magnetite/alum or haematite/ferric systems in order to produce a combined approach for maximising membrane throughput and organics removal.
8. Modelling and Desk Studies

The filtration of water using hollow fibre microfiltration membranes has arguably become an industry-wide standard. The water flow through these hollow fibres presents some unique hydrodynamic properties that influence the shape of the membrane flux versus throughput curves, produced when using these membranes. A model was developed which related the hydrodynamics of water flow through hollow fibres to the fouling of these fibres by particulate deposits (Publications 2 and 4 and CSIRO Internal Report FE-79).

Desk studies were performed in order to determine the benefits of the hybrid membrane processes relative to the use of direct dosing of alum onto microfiltration. The magnetite/alum hybrid system yielded the best improvement in membrane throughput and so was analysed in these studies. The desk study aimed to determine whether, and at what level of membrane performance improvement was the added cost associated with the use of the hybrid magnetite/alum process justified in terms of savings in membrane backwashing and chemical cleaning.

8.1 Method

8.1.1 Hydrodynamics of Hollow Fibre Membrane Filtration and Fouling

Microfiltration experiments were carried out on polypropylene hollow-fibre membranes using the filtration apparatus shown in Figure 1. The fibres had a nominal pore size of 0.2\( \mu \)m, an internal diameter of 250\( \mu \)m and an external diameter of 550\( \mu \)m. The fibres were originally 1.2m long and were cut to several shorter lengths. Filtration occurred from the outside to the inside of the fibre. Fibres were opened at both ends and sealed at the outer wall by threading the ends through a silicone septum. The fibres were then wet and degreased with ethanol, and flushed thoroughly with MilliQ water. The feed stream was prepared in a stirred vessel and pumped onto the membrane with a peristaltic pump (Watson-Marlow). The feed was forced through the hollow-fibre membrane under pressure and permeate emerged from the opened ends. The permeate was collected in a vessel mounted on an analytical balance (A&D). Feed pressure was measured by a pressure transducer and allowed to follow the peristaltic pump curve uncontrolled. The signals from the analytical balance (WT) and pressure transducer (PT) were processed with data acquisition software (Genie) to calculate the permeate flow rate as a function of permeate throughput. The importance of axial features in determining filtration behaviour in pure systems was investigated using MilliQ water. The importance in determining fouling behaviour was investigated using a 100mg/L suspension of montmorillonite (SWy-2) in MilliQ water.

The membrane permeability was determined experimentally in order to calculate the characteristic length \( \frac{d^2}{k} \sqrt{\frac{\pi}{128\eta}} \) of the hollow-fibre membrane used. This length was used to predict the effect of fibre dimensions on the permeate flow rate, flux profile, and on membrane fouling. Permeate flow rates were measured experimentally as a function of fibre length and surface area. The role of axial features in productivity and fouling was then inferred from the model predictions and experimental observations.

8.1.2 Desk Studies

The costs for chemical cleaning of microfiltration membrane systems were based on data provided by Melbourne Water for their 6ML/day microfiltration plant operating with alum pre-treatment at Cresswell, near Healesville, Victoria.

8.2 Results

8.2.1 Hydrodynamics of Hollow Fibre Membrane Filtration and Fouling
The effect of fibre length (Publications 2 & 4 and CSIRO Internal Report FE79) on the permeate flow rate was determined by filtering MilliQ water through membranes of various lengths. The experimentally determined permeate flow rate \( Q_p \) as a function of fibre length \( L \) is shown in Figure 22, together with that predicted from theory. The permeate flow rate increased with fibre length up to 0.2m, and then was independent of fibre length above 0.2m. If the minimum fibre length is taken as the shortest length (minimum surface area) for which the maximum permeate flow rate is achieved, then this length is approximately 0.2m, for the type of membrane used. Increasing fibre length beyond 0.2m reduced permeate flow rate per unit surface area.

8.3 Discussion

8.3.1 Hydrodynamics of Hollow Fibre Membrane Filtration and Fouling

The fouling of hollow-fibre membranes progresses through three distinct regimes characterised by changes in the dependence of fouling rate on fibre length and surface area. Fouling regimes are caused by distinct patterns of particle deposition onto the membrane surface, which change as fouling progresses. These dynamic patterns are in turn caused by the non-uniform axial flux profile, which depends upon the membrane permeability, fibre length and diameter. Fouling behaviour is inferred from the decline in permeate flow rate during microfiltration through fibres of various lengths and surface areas.

The initial fouling regime is characterised by a decline in permeate flow rate which is independent of fibre length and membrane surface area. In a non-fouling system the flux is highest at the open end of the fibre. In a fouling system, deposition onto the membrane surface is initially greatest at the open end, however, for fibres longer than the minimum length (0.2m in this case), the flux profiles are similar over an area that extends back from the open end of the fibre. The pattern of deposition and the rate of fouling are independent of fibre length within this region. Deposition is initially greatest where the flux is highest, so the most productive region of the membrane is fouled first. Accordingly, the initial decline in permeate flow rate is more severe for a hollow fibre than for a planar membrane of the same surface area.

The experimental observations and the model predictions point towards the three separate fouling regimes. In the initial regime, the rate of fouling is insensitive to fibre length. In the
intermediate regime, the rate of fouling is lower in longer fibres. In the final regime, the rate of fouling depends on membrane surface area (and therefore also on fibre length). More detail on the modelling and fouling results can be found in Carroll, T. and Booker, N.A.: “Axial features in the fouling of hollow fibre membranes.” (Publication 4)

8.3.2 Desk Studies

The increased costs of the magnetite-alum pre-treatment system were compared to the reduced cleaning costs for a microfiltration plant using only alum pre-treatment. Figure 23 shows the cost of the magnetite/alum system as a function of plant throughput and compares that to the cost of chemical cleaning of the membrane. The comparison was based upon the assumption that the benefit of a higher membrane throughput would be reduced chemical cleaning frequency. Backwash frequency (and the associated downtime, reduction in product water yield, and energy consumption) was assumed to be unaffected. The capital and operating costs of the magnetite recovery plant were not considered.

![Figure 23: Comparison between reduced cleaning costs and increased treatment costs associated with a hybrid alum-magnetite pre-treatment system.](image)

The chemical cleaning costs were taken from a 6ML/day microfiltration plant operating with alum pre-treatment at Cresswell, near Healesville, Victoria, Australia. The additional treatment costs include sodium hydroxide for magnetite regeneration, polyelectrolyte for magnetite-alum flocculation, and magnetite to replace unrecovered losses.

From Figure 23 it can be seen that twice the microfiltration membrane throughput was required before the savings in cleaning costs balance the increased cost of the magnetite-alum pre-treatment system. The laboratory magnetite/alum trials, as shown in Figure 18a indicate that this throughput increase could be achieved with a magnetite dose of 1.0 g/L and an alum dose of 3.2mg/L Al.

The pilot plant results shown in Figure 20, indicate however, that membrane throughput was improved by about 1.5 to 2 times compared to that of alum alone. From Figure 23, it can be seen that this level of performance improvement was insufficient to justify the increased cost of the magnetite/alum hybrid system. Therefore, although the laboratory trials indicate that the magnetite/alum system looked promising, the pilot plant work did not confirm this.

The difference in performance between the laboratory and pilot plant for the magnetite/alum hybrid system was probably a result of differences in kinetics and/or shear between the two scales of operation. It is likely that localised areas of high shear in the pilot plant could have resulted in detachment of the alum floc from the magnetite particle surface. Although every effort was taken to minimise velocity gradients between the contact stage and the membrane, some detachment of floc was observed. This was evidenced by visual observations of some free floc in the membrane feed water. The presence of these
unattached alum floc in the membrane feed would have resulted in fouling of the membrane surface, similar to that observed when alum was used alone. Designing a process where velocity gradients are kept to a minimum whilst still providing the pressure gradient necessary to operate the membrane filtration step will be difficult. As a result, it was concluded that the hybrid magnetite/alum process was unlikely to be economically viable when compared to direct dosing of alum before microfiltration.

8.4 Conclusions

8.4.1 Hydrodynamics of Hollow Fibre Membrane Filtration and Fouling

The use of hollow-fibre membranes for filtration introduces axial features that have implications for the rate and mechanism of membrane fouling. A non-uniform axial flux profile is ubiquitous in hollow-fibre filtration, and leads to a non-uniform pattern of foulant deposition. Fouling occurs first in a region of the membrane where the flux is highest and the resultant decline in permeate flow rate is larger than for fouling of a region of lower flux. As a result, the rate of fouling of a hollow-fibre membrane is initially faster than for a planar membrane configuration. Furthermore, regions of the membrane where the flux is initially negligible begin to contribute as fouling proceeds. As a result, the axial flux profile becomes progressively more uniform.

Fouling of a hollow-fibre membrane appears to progress through three distinct regimes, as deduced from the fouling behaviour of a clay suspension as a function of membrane length. A simple model of fouling which considers only membrane permeability, and fibre length and diameter is useful to isolate the contribution due to axial features, and to understand the different mechanisms of fouling in the three regimes. In the initial regime, the rate of fouling is independent of fibre length and surface area. As fouling proceeds into the intermediate regime, the rate of fouling is lower for longer fibres. Axial features are significant in these two regimes. Eventually, in the final regime, after a substantial decline in permeate flow rate, the rate of fouling depends on membrane surface area rather than fibre length, and axial features are less significant. It is important to include these effects in both hollow-fibre module design, and in understanding the causes and effects of fouling.

8.4.2 Desk Studies

The study into the relative advantages of the hybrid magnetite/alum process compared to alum coagulation as a pre-treatment before MF showed that the throughput of the membrane process would need to be at least doubled for the increased operating cost to balance the savings in chemical cleaning. Although the magnetite/alum hybrid system exhibited the ability to extend throughput by a factor of four or more in the laboratory tests, this was not achieved at the pilot plant scale. Scale up effects such as velocity gradients increasing shear on the magnetite particles were thought to be responsible for this deterioration in performance.
9. Surface Modified Membranes

Removal of NOM via adsorption was investigated in earlier sections 4, 6 and 7, and proved to be effective. However, the adsorption processes investigated did not remove the hydrophilic neutral NOM and this was shown to be a major membrane foulant. In this section, polypropylene membranes were grafted with polymer coatings in an attempt to increase the NOM rejection of microfiltration membranes. Neutral, positively charged and negatively charged polymer coatings were grafted onto the polypropylene membranes, and the rate of flux decline was measured as a function of grafting conditions. Details of the grafting conditions and the preliminary membrane performance results are more fully detailed in Publications 7, 8 and 9.

Those grafting conditions that produced the most promising results were evaluated in extended laboratory trials, so that the long-term performance of grafted membranes could be evaluated. The extended laboratory trials included backwashing and chemical cleaning, so that the effect of these operations on the long term performance of grafted membranes was included in the experiments. A detailed description of these experiments and results is given in CSIRO Internal Report FE-95.

9.1 Method

9.1.1 Membrane preparation

Polypropylene hollow-fibre microfiltration membranes were modified (nominal pore size = 0.2 µm, an internal diameter = 250 µm, an outer diameter = 550 µm, length = 0.9 m, nominal surface area = 7 cm²). The coating process involved the formation of functional sites on the membrane surface, following which polymers are grafted onto the membrane surface via these functional sites. Anionic, cationic or non-ionic polymers were then grafted onto the polypropylene membranes by immersion of the membranes in monomer solutions of various concentrations for predetermined polymerisation times. Negatively charged surfaces were grafted from acrylic acid (AA) monomer solutions, positively-charged polymers were grafted from 2-(N,N-dimethylamino)ethyl methacrylate (DMAEMA) monomer solutions and neutral hydrophilic polymer was grafted from poly(ethylene glycol)₉₀₀ monomethyl ether monoacrylate (PEGMA) monomer solutions. The chemical structures of the monomers are given in Figure 24. The membranes were washed and dried following the polymer coating process and the graft yield for each membrane fibre calculated from the weight gain. The virgin polypropylene membrane is denoted PP, and the modified membranes are denoted PP/-, PP/+ and PP/0, for the AA, DMAEMA and PEGMA grafts respectively.

Figure 24: Chemical structure of monomers used for grafting; A) Acrylic acid, B) 2-(N,N-dimethylaminoethyl) methacrylate, and C) Poly(ethylene glycol)₉₀₀ monomethyl ether monoacrylate

A) \[ H_2C\text{C=CH}_2 \]  
B) \[ \text{CH}_3\text{CO}_2\text{H} \]  
C) \[ \text{CH}_2\text{CH}_2\text{O}[\text{CH}_2\text{CH}_2\text{O}]_{16}\text{CH}_3 \]

9.1.2 Preliminary Laboratory Investigations

Microfiltration experiments were carried out on non-grafted and grafted single polypropylene hollow-fibre membranes using the laboratory single fibre test rig (section 3.1). The raw water source was the Moorabool River near Anakie, Victoria, Australia. This water has a dissolved organic carbon (DOC) concentration of 9.0 ppm, a turbidity of 4.3 NTU, a pH of 7.4 and a calcium concentration of 10 mg/L as CaCO₃ equivalents. The raw water was filtered both untreated and after coagulation pretreatment with alum. In the former case, the pH was adjusted to 6.5 before filtration. In the latter case, alum was dosed...
at 5.0mg/L (as Al\(^{3+}\)), the pH was adjusted to 6.5, and the water was filtered after a 5min. maturation period. The effect of water hardness was investigated by adding calcium chloride to the raw water (adjusting to pH 6.5) at concentrations of 100 and 350 mg/L as CaCO\(_3\) equivalents. The raw water was rated soft, and the two artificially hardened waters are rated moderately hard and hard respectively.

9.1.3 Extended Laboratory Investigations

The experimental procedure for the extended laboratory investigations were similar to those for the preliminary investigations, except that the micro-filtration experiments were run over extended time frames and included air backwashing and chemical cleaning (Memclean or 5% Decon90) of the membranes. Further details of the experimental apparatus and experimental procedures are given in CSIRO Internal Report FE-95.

The raw water source was permeate from the Yarra Glen microfiltration water treatment plant, Victoria. The Yarra Glen water treatment plant takes water from the Maroondah aqueduct, coagulates with alum and filters the water through a 0.2 µm polypropylene microfiltration plant. Therefore, the permeate was free of particulates and NOM that is removable by coagulation. Previous work had shown that NOM not removed by coagulation would be retained in the permeate and that this NOM fraction was the most problematic with regards to membrane fouling. This allowed the experiments to focus on the NOM fouling of the coated membranes with reduced laboratory preparation of the waters.

9.2 Results

9.2.1 Preliminary Experiments

Permeability of grafted membranes

Grafting of polymers onto the polypropylene membranes led to reduced membrane permeability, and the permeability of the membranes reduced as the extent of grafting increased (Figure 25). Grafting of the polyelectrolytes reduced the effective membrane pore size, and the grafting process precluded the possibility of any compensating permeability enhancement from structural damage.

Figure 25: Effect of graft yield on water permeability for a PP/- membrane (○) and a PP/+ membrane (□)

The permeability of membranes grafted with charged polymers was dependent upon the pH, as shown in Figure 26. Changes in the permeability of grafted membranes may be explained by considering changes in polymer chain conformation with pH, and this is detailed in Carroll, Booker and Meier-Haack [Publication 7]. When the chain conformation is extended (high pH for negatively charged polymers and low pH for positively charged polymers), the polymer lies flat on the membrane surface and blocks more pores than when it is coiled. Thus, the permeability of the grafted membranes is higher at pH values that
induce the polymer chains into coiled conformations, and this is represented diagrammatically in Figure 27. The hysteresis shown in Figure 6 also suggests that the stretched polymer conformation is stabilised by adsorbed counter ions until the pK_a of the polyelectrolyte is reached.

Figure 26: Effect of pH on pure water flux for an ungrafted membrane (○), a PP/+ membrane 16.9 % w/w graft yield (□) and a PP/- membrane 6.2 % w/w graft yield (◇)

Figure 27: Schematic drawing of the effect of pH on the chain conformation of grafted polyelectrolytes.

The conformation of polyelectrolytes may also be altered by the adsorption of counter ions. Exchange of Na^+ ions for protons on the acrylic acid polymers decreased the membrane permeability (30% decrease), and this was ascribed to the higher space demand of the comparatively bulkier sodium ion leading to a widening of the grafted polymer chains and therefore to a decreasing pore size and a decrease in permeate flux. Divalent ions, such as Ca^{2+} and SO_4^{2-}, form multivalent complexes with the charged groups of the grafted polymer chains and build-up a network of physical crosslinks (bridging effect) within the grafted layer. This complexation forces the polymer chains into a compact conformation, as shown in Figure 28. The compaction of the polymer chains increases the pore size and thereby increases the permeate flux, and this was observed for both the polyacrylic acid/Ca^{2+} system and the PP/+/SO_4^{2-} system.
Figure 28: Schematic drawing of the effect of divalent calcium ions on the conformation of grafted polyacrylic chains.

Fouling of modified membranes by NOM

The flux declines versus throughput for Moorabool NOM filtered through PEGMA-grafted membranes (PP/0), DMAEMA-grafted membranes (PP/+) and acrylic acid grafted membranes (PP/-) are shown as a function of graft yield in Figures 29, 30 and 31. The flux decline versus throughput for the ungrafted membrane is also shown for comparison.

The rate of flux decline with throughput was substantially lower for the PP/0 and PP/+ grafted membranes than for the ungrafted membrane, and both the PP/0 and PP/+ membranes displayed minimum flux decline rate as a function of graft yield. The optimum graft yield for PP/0 grafted polymers was 5.2% and for PP/+ grafted polymers was 11.3%.

The flux declines versus throughput for Moorabool NOM filtered through PP/- grafted membranes were the same as the ungrafted membranes at low graft yields (3.8 % w/w). As the graft yield increased, the initial flux was lower than the ungrafted membranes but increased to about the same flux as the ungrafted membranes before declining. In some instances there was a slight improvement over the ungrafted membranes at high permeate throughputs.

A more detailed discussion of the mechanisms for the change in flux decline are given in Publication 7.

Figure 29: Effect of nonionic grafting on the fouling by NOM for various graft yields.
Figure 30: Effect of cationic grafting on the fouling by NOM at pH 7.4 for various graft yields.

Figure 31: Effect of anionic grafting on the fouling by NOM at pH 7.4 for various graft yields.

Permeate quality of modified membranes

The NOM rejection as a function of graft yield was measured as the difference in UV-absorbance of feed and permeate at 254 nm. The average $\text{UV}_{254}$ removal was approximately 7%, and there was no significant difference between grafted and ungrafted membranes, with the exception of the highest PP/+ graft yield (20.7 % w/w) which had $\text{UV}_{254}$ removal of 14%. The invariance of $\text{UV}_{254}$ removal to grafting is consistent with the stability of membrane polymer backbone bonds under the thermally-activated chemically-initiated grafting process. The commonly-reported trend of increased rejection with reduced permeability was confined to a single case, perhaps because the grafted layer permeability decreased as filtration proceeded. The consistent permeate quality across the selection of grafted polymers at various graft yields reflects the role of both hydrophilization and layer compaction in countering the effects of fouling, as opposed to changes in the rejection characteristics of foulants.

9.2.2 Extended Membrane Experiments

The PP/0 and PP/+ grafted membranes appeared to offer the best possibility for reducing the flux decline of polypropylene membranes, and membranes with graft yields of 3.2%-4.9% w/w PP/0 and 9.4%-12.6% w/w PP/+ were used in the extended filtration studies. The initial flowrate through the membranes was measured with MilliQ water and the results are shown in Table 10. There was no difference between the initial flowrates of grafted and non-grafted membranes.
### Table 10: Clean membrane permeability

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<td>% error</td>
<td>5.336</td>
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There was a small decrease in the fouling rate for the PP/0 and PP/+ grafted membranes in some instances, and no difference in the flux recovery after backwashing between grafted and non-grafted membranes. This indicates that there is a minor reduction in the initial NOM fouling of grafted membranes compared to non-grafted membranes, and that backwashing of NOM does not result in flux recovery.

The effect of chemical cleaning of PP/+ grafted and non-grafted membranes are shown in Figure 32. The standard or non-grafted membrane performed better after chemical cleaning with 5% Decon90, while the performance of the PP/+ grafted membrane decreased after chemical cleaning. Furthermore, the performance of the PP/+ grafted membrane was the same or worse than that of the non-grafted membrane. Similar results were obtained for the PP/0 grafted membranes. The polymer grafted membranes were unable to significantly reduce fouling and their performance was adversely affected by chemical cleaning.

**Figure 32: Comparison between PP/+ and non-grafted membranes in extended trials and following chemical cleaning.**

![Membranes before and after cleaning with 5% Decon90](image)

### 9.3 Conclusions

Grafted membranes showed some tendency towards reduced NOM fouling rates in short term trials. However, comparison of grafted and non-grafted membranes demonstrated that any reduction in membrane fouling with grafting was small and short lived, as chemical cleaning of the grafted membranes reduced their fouling performance.
10. Floc Structure

Andrew Lee at UNSW investigated the effect of floc properties on the performance of membranes in water treatment. Previous research data show qualitative agreement with a simple model based on the Carman-Kozeny equation. Larger flocs form more porous cakes than smaller flocs and thus achieve higher fluxes due to their larger inter-floc porosity. Similarly, looser flocs are likely to form a cake that has higher intra-floc porosity giving fluxes higher than a cake made of compact flocs if they have similar size. This work investigated the flocculation of hematite particles in the absence and presence of humic acid on floc structure and membrane performance.

Flocculation and microfiltration of hematite in the absence of humic acid

This work, in the absence of organic material, demonstrated that there are two factors that influence flux in the microfiltration of flocculated particles, i.e. a major floc size effect and a minor floc structure effect. Recent data illustrate that the structural effect cannot be underestimated because structural factors such as fractal dimension (dF) give information on compression phenomena. It has been found that the structure of flocs is related to the compressibility of the cake formed on the membrane surface (low values of dF show increased compressibility) whereas no size effect on compressibility is found. Thus, it was observed that large flocs with loose structure had higher fluxes for low trans membrane pressure (TMP) compared with smaller, more compact flocs, while the reverse was true for high TMP. Therefore, microfiltration of large, loose flocs is best performed under low TMP (<10 kPa), while more compact flocs show the best results at higher TMP (>10 kPa). Details of this work are given in publications 20 and 21.

Flocculation and microfiltration of hematite in the presence of humic acid

Hematite particles were flocculated by two different protocols. (1) Hematite was flocculated by KCl then humic acid was added into the solution when floc size reached more than 8 µm (SPO procedure, sequence is salt-particle-organic). (2) Humic acid was dispersed with hematite particles in water and KCl added into the solution to induce flocculation (OPS procedure, organic-particle-salt).

Experimental results showed that OPS flocculation took longer than SPO flocculation at the same concentration of humic acid and showed slightly higher adsorption of humic acid onto the hematite particles. The fractal dimension (dF) of flocs was influenced by the humic acid concentration and flocculation protocols. OPS flocs tended to have clearly identifiable low dF values at the low humic acid concentration whereas dF analysis of flocs was difficult at high concentrations of humic acid.

It was found that OPS flocs had higher specific cake resistances and sharper flux declines due to their compression, when they formed a cake during dead-end microfiltration (Figure 33).

The SPO flocculation procedure was a more effective way to remove humic acid from water due to its faster flocculation kinetics, ability to tailor floc size and structure, and the lower resistance and compressibility of the cakes formed. The only apparent advantage of the OPS protocol is the 10 to 20 % higher adsorption of humic acid onto the hematite particles.
Figure 33: Specific cake resistance vs TMP for SPO and OPS flocculation regimes.
11. Overall Conclusions

The project started later than the original timelines suggested due to delays in appointing the appropriate research scientists to the CSIRO component of the project. A change in project timing was requested from the CRC Management Committee and approved so that the project commenced at the beginning of November 1997. Based on the revised start time, the project successfully completed most of the targeted milestones to the agreed schedule.

The project aim of developing a hybrid membrane process that would be suitable for small remote water treatment plants was not achieved. However, the project outcomes have led to a greater understanding of the factors influencing the operation of microfiltration membranes used in Australian drinking water treatment plants and indicated a number of possible future directions for improvements to these processes.

An analysis of the different coagulants available for water treatment, in combination with microfiltration, showed that alum gave as good as, if not better, performance than all the other inorganic coagulants tested. The only exception to this was a possible improvement in backwash efficiency with the pre-polymerised aluminium coagulants, when compared to alum. Whether this improvement in membrane backwash efficiency warrants the increased cost of the pre-polymerised aluminium coagulants was not determined.

Attachment of alum or ferric sulphate coagulated natural organic matter to the surface of hard particles such as magnetite or powdered activated carbon will result in improved membrane throughput. The effects of shear on the hard particle/chemical floc structure need to be controlled to ensure the benefits of this approach are realised. Through this approach, particulate fouling of microfiltration membranes can be minimised and membrane performance is then dominated by fouling caused by the residual organics.

The specific fraction of the dissolved organic matter present in Australian surface water that was responsible for the majority of the fouling on hydrophobic microfiltration membranes, after particulate fouling was eliminated, was identified. This was shown to be the low molecular weight fraction of the neutral hydrophilic organics. This fraction was not removed by conventional inorganic coagulation processes or by the adsorbent materials most commonly used in water treatment or by combinations of the two. Further work is required to identify a suitable process or mechanism for removing this specific fouling fraction from water prior to microfiltration processes.

The best hybrid membrane approaches identified in this project were the magnetite/alum and haematite/ferric systems as these were capable of improving membrane throughput by about a factor of two compared to direct dosing of alum into the membrane feed stream. Analysis of the process economics of the hybrid membrane systems demonstrated that an improvement in membrane throughput of this order of magnitude was insufficient to justify the added cost and complexity of these hybrid approaches.

Surface modification of the hydrophobic, polypropylene, hollow-fibre membranes that are currently used in microfiltration processes in Australia showed a reduced rate of fouling by NOM in preliminary experiments. However, long term laboratory experiments demonstrated that there was no significant difference in membrane fouling or permeate quality between the grafted and non-grafted membranes.
12 Future Research

During the completion of the membrane project some promising project areas were identified that may have significant benefit to membrane users and the water industry. These include the modification of the membrane surface to enhance organics rejection, submerged membrane systems and a comparison to ultrafiltration for NOM removal.

12.1 Submerged membrane systems

Submerged membrane systems such as the Zenon, ZeeWeed® system and the MEMCOR Garrow system are emerging as lower cost systems for membrane filtration of raw water. They offer significant advantages for “engineering” some of the hybrid membrane processes that have been developed in this CRC for Water Quality & Treatment project. It is proposed that a small laboratory scale submerged membrane unit be built to test the potential of the hybrid membrane systems in this form of membrane separation unit. This would then link to larger scale pilot plant trials with one of the above mentioned membrane manufacturers, to test the hybrid membrane approaches in the field.

12.2 Ultrafiltration

At the fifth year CRC for Water Quality & Treatment project reviews, the external reviewer for Programme 3, Prof. Hallvard Odegaard, recommended that the hybrid approaches developed within this project, be “bench-marked” against ultrafiltration, the most commonly used membrane process in Europe for NOM removal. This would best be performed at the pilot plant scale, in collaboration with suitable membrane manufacturers, and involve a long term continuous trial of the best of the hybrid approaches (eg. magnetite/alum) versus a typical ultrafiltration system, preferably using hydrophilic membranes.
Publications and Reports

CSIRO Internal Reports:

FE-72 Carroll, T, Oct. 1998: “Microfiltration performance of selected adsorbents compared to alum and PACI flocs”


FE-77 Booker, N. Jan. 1999 FE-77: “Preliminary combined MIEX® resin/alum coagulation microfiltration membrane tests”


FE-80 Carroll, T. and Booker, N., May 1999: “Fouling of drinking water membranes by fractionated natural organic matter”


FE-83 Carroll, T. and Booker, N. June 1999: “Comparison of micro-filtration performance of several aluminium and iron based coagulants”

FE-95 Bridger, J.S., June 2002: “Extended laboratory testing of polymer grafted membranes.”

Publications


**Research Student Theses**


Fan, L., 2002, “Interactions of Natural Organic Matter (NOM) and Microfiltration Membranes in Potable Water Treatment.” PhD in Chemical Engineering

Lee, A., To present for PhD in Chemical Engineering, UNSW

References


(5) Personal communication – Barwon Water operators at the Meredith MF membrane treatment plant

APPENDIX 1

Proposed Project Milestones

The milestones that were planned for the project in the initial project proposal are shown in the following table.

<table>
<thead>
<tr>
<th>Date</th>
<th>Milestone</th>
<th>Indicator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nov'97</td>
<td>Appoint suitable R&amp;D staff to CSIRO</td>
<td>Staff appointed</td>
</tr>
<tr>
<td>Feb'98</td>
<td>Design and construct lab MF unit</td>
<td>Ready to start lab trials</td>
</tr>
<tr>
<td>Mar'98</td>
<td>Fill RMIT PhD scholarship position</td>
<td>Student selected and enrolled at RMIT</td>
</tr>
<tr>
<td>Mar'98</td>
<td>Set up procedure for pre-concentrating water samples for laboratory analysis and experimentation</td>
<td>Purchase and commissioning of R/O unit</td>
</tr>
<tr>
<td>Apr’98</td>
<td>Establish sampling/analysis protocol for operating MF units</td>
<td>Melbourne Water Corporation collaboration in place</td>
</tr>
<tr>
<td>Apr’98</td>
<td>Determine effect of particle size and dose on MF membrane flux</td>
<td>Acceptable operating range for MF</td>
</tr>
<tr>
<td>Apr’98</td>
<td>Selection of suitable target water types for lab studies</td>
<td>Meet typical spread of quality types.</td>
</tr>
<tr>
<td>May’98</td>
<td>Development of procedure to study floc structure interactions on MF</td>
<td>Size and strength measurements</td>
</tr>
<tr>
<td>July’98</td>
<td>Selection of suitable adsorbents to study in lab and pilot plant</td>
<td>NOM removal potential vs MF performance</td>
</tr>
<tr>
<td>Sept’98</td>
<td>Select required membrane process on which to apply hybrid processes in pilot trials</td>
<td>Suitable membrane unit sourced for pilot plant trials</td>
</tr>
<tr>
<td>Oct’98</td>
<td>Design, construct &amp; commission flexible pilot plant facility suitable for use at remote locations.</td>
<td>Unit built and ready for use</td>
</tr>
<tr>
<td>Nov’98</td>
<td>Complete screening of currently available adsorbents e.g. clays, resins, oxides for use in MF</td>
<td>Selection of most appropriate adsorbent/MF combination</td>
</tr>
<tr>
<td>Nov’98</td>
<td>Complete testing of commercially available coagulants and flocculants in conjunction with MF</td>
<td>Selection of most effective coagulant/MF combination</td>
</tr>
<tr>
<td>Nov’98</td>
<td>Selection of suitable sites for pilot plant test work</td>
<td>Suitable water quality, quantity and geographic location</td>
</tr>
<tr>
<td>Jan’99</td>
<td>Technical and economic comparison of hybrid approach to conventional and emerging alternative technologies</td>
<td>Decision to proceed with current approach or to develop new reagents</td>
</tr>
<tr>
<td>Feb’99</td>
<td>Synthesis &amp; testing of new adsorbents &amp; polymers</td>
<td>Cost effective alternative to commercially available systems</td>
</tr>
<tr>
<td>Nov’99</td>
<td>Selection of best combination MF system</td>
<td>Best organics removal from water at least cost.</td>
</tr>
<tr>
<td>Mar’00</td>
<td>Completion of pilot plant tests of most effective adsorbent/coagulant/MF combinations</td>
<td>Optimum performance conditions determined</td>
</tr>
<tr>
<td>May’00</td>
<td>Complete technical and economic evaluation of process</td>
<td>Full cost and performance assessment</td>
</tr>
<tr>
<td>June’00</td>
<td>Final report and recommendations</td>
<td>Process design and selection criteria specified</td>
</tr>
</tbody>
</table>
The Cooperative Research Centre for Water Quality and Treatment is an unincorporated joint venture between:

- ACTEW Corporation
- Australian Water Quality Centre
- Australian Water Services Pty Ltd
- Brisbane City Council
- Centre for Appropriate Technology Inc
- City West Water Limited
- CSIRO
- Curtin University of Technology
- Department of Human Services Victoria
- Griffith University
- Melbourne Water Corporation
- Monash University
- Orica Australia Pty Ltd
- Power and Water Corporation
- Queensland Health Pathology & Scientific Services
- RMIT University
- South Australian Water Corporation
- South East Water Ltd
- Sydney Catchment Authority
- Sydney Water Corporation
- The University of Adelaide
- The University of New South Wales
- The University of Queensland
- United Water International Pty Ltd
- University of South Australia
- University of Technology, Sydney
- Water Corporation
- Water Services Association of Australia
- Yarra Valley Water Ltd