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# COLOUR REMOVAL WITHOUT CHEMICAL ADDITION USING NANOFILTRATION

***Paper Presented by :***

**Eddy Ostarcevic**

***Author:***

**Eddy Ostarcevic,** *Treatment & Distribution Manager,*

Grampians Wimmera Mallee Water

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# COLOUR REMOVAL WITHOUT CHEMICAL ADDITION USING NANOFILTRATION

**Eddy Ostarcevic**, *Treatment & Distribution Manager*, GWMWater

## ABSTRACT

The 2005 Kwatye (Water) Prize awarded by WIOA and sponsored by Environmental & Process Technologies provided an outstanding opportunity to investigate an alternative treatment process to remove natural organic matter (NOM), that generally colours raw water supplies, without the need to add metal salts such as aluminium sulphate.

The Australian experience in reducing colour is largely through the use of one or more conventional treatment steps such as coagulation, flocculation, sedimentation, flotation, media or membrane filtration. The difficulty with these conventional processes include limited removal of the NOM leading to the production of disinfection byproducts, a continued supply of food for the production of biofilms in distribution networks, increasing the disinfectant demand and the need to introduce chemicals such as aluminium salts into the treatment process.

Nanofiltration has been used to deliver finished water with low NOM, and consequently colour, in various countries throughout the world. Membrane technology has provided another set of tools to deliver safe drinking water to our communities. The Kwatye (Water) Prize provided the opportunity to visit researchers, membrane manufacturers and water treatment plants in USA, Scotland, and Europe to learn from their experiences.

## 1.0 INTRODUCTION

The Kwatye (Water) Prize awarded during the WIOA conference in 2005 provided an outstanding opportunity to investigate the opportunity to visit water supplies using nanofiltration to remove dissolved organic matter from raw water. Visits to membrane manufacturers, researchers and operators were organised in USA, UK and Europe to understand the design and operational characteristics of nanofiltration membrane systems.

Colour is generally used throughout the water industry as the parameter of choice to determine whether treatment has been effective. However, by understanding that colour is an indicator of only some of the components of the organic content of water opens up the question of the effectiveness of conventional treatment processes with respect to NOM removal. NOM that remains in the treated water does have an impact on the formation of disinfection by products (DBP) and biofilm growth in the distribution network. Understanding the variety and nature of NOM, and the effect that treatment has on various components of NOM, helps to define the impact on the finished water quality and in the distribution network.

Coloured water that contains little alkalinity and that is considered soft and aggressive presents a challenge to water authorities to provide a safe drinking water.

Soft coloured water supplies currently require chemical treatment to convert the dissolved organic carbon compounds (DOC) into particulate material so that it can be removed by using one or more of the conventional treatment steps available such as coagulation, flocculation, sedimentation, flotation, media or membrane filtration.

Low alkalinity water sources require preconditioning using pH correction to ensure that the coagulation and flocculation processes are optimised. However, no matter how well the water is preconditioned and chemically coagulated a recalcitrant portion of the dissolved organic matter will continue to remain in the water.

The level of recalcitrant material remaining in the treated water supply depends on the characteristics of the natural organic matter that dissolves into the water as the water is harvested from the catchment. The remaining dissolved organic material after treatment will generally combine with the chemical used to disinfect the drinking water supply thereby requiring higher doses to overcome the demand and inevitably form disinfection byproducts. Elevated DBP levels may also exceed the drinking water standard adopted in Victoria and used as a guideline in the Australian Drinking Water Guidelines throughout Australia.

Another major consideration with the conventional method of removing colour, thereby reducing the NOM, from drinking water supplies includes the desire of communities to reduce or eliminate chemicals in the production of their drinking water supply.

GWM Water has undertaken extensive community consultation throughout the region it serves and the key message from our customers is that they want to reduce or eliminate the use of chemicals. Our community consultation program aims to educate our customers so that they are able to make informed decisions so they understand that disinfection is critical and while they may not like the addition of disinfectant they generally accept it as a necessity. GWM Water's customers are not unique as evidence of the desire to minimise chemical addition to water supplies is a concept generally shared by other communities across the state and throughout Australia.

Membrane manufacturers such as Hydranautics, Koch Membranes, Dow FilmTec and PCI have all developed membranes capable of removing dissolved organic carbon from raw water. Nanofiltration (NF) and some ultrafiltration (UF) membranes have become part of a wider set of tools that can be used to reduce NOM in drinking water. The questions that require further study to determine what applications suit these membranes best include the following.

1. What recovery rate is sustainable for UF and NF using different DOC sources such as that typically found in Tasmania, tropical north Queensland and the Northern Territory and the mountain regions of Victoria and NSW.
2. Can NF and UF membrane system operate with recovery rates as high as 95%?
3. Can increasing raw water temperature enhance DOC removal?
4. What type of fouling problems will be generated?
5. Will these membranes be subject to increased microbial fouling because of the concentrated food source available?
6. What are the limitations in water quality with respect to the types of DOC and alkalinity concentrations as well as calcium hardness?
7. Can the concentrated DOC be used as a soil conditioner when the raw water supply is soft? Can this equally apply to hard coloured water sources?

This paper will provide some answers to these questions and some case studies of water treatment using nanofiltration.

## 2.0 COLOUR AND NATURAL ORGANIC MATTER (NOM)

NOM is the general term used to describe a broad group of organic compounds found in all waters, whether derived from catchments as surface water or from ground water sources. NOM may also include organic matter generated by domestic, industrial or agricultural sources. NOM can be highly variable based on seasonal differences and can contain a diverse range of materials that make up a complex character that is unique for each water source.

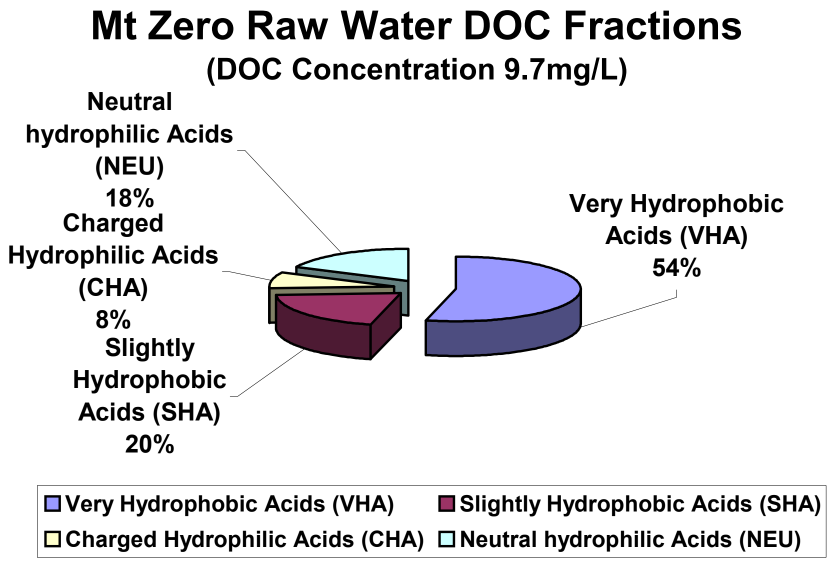
Decay and leaching of organic materials from plants, animals and microorganisms and the subsequent transport of these compounds into the water is the primary source of NOM (Pelekani et al. 1999). Some of the compounds that contribute to the character of NOM (Prévost et al. 2005) include:

- The constituents of microorganisms in the natural environment such as proteins and amino acids.
- Polysaccharides and amino sugars that are structural components of cell walls.
- Lignins, tannins and fulvic acids.

Some of the components of NOM such as tannins and fulvic acids contribute to the colour of water whereas polysaccharides do not affect the colour of water. Coagulation using metal salts removes a portion of NOM in water; typically 30% – 60% but removal rates are dependent on the character of NOM and the performance of the treatment process.

NOM primarily consists of carbon, oxygen, nitrogen, hydrogen and sulphur all bound together in a complex array of compounds. Organic carbon may represent up to 50% of NOM and can be in either particulate or dissolved forms. Total organic carbon (TOC) and more particularly dissolved organic carbon (DOC) are used as an indicator of NOM in water at various stages of drinking water production.

Some specific components of DOC can be separated, based on their physical properties, to better characterise NOM in the water and identify the likely outcome of treatment. The specific fractions of DOC in the Mt Zero raw water are shown below.




Mt Zero WTP provides drinking water to the community of Horsham and it is the largest DAFF treatment process that GWM Water operates. The VHA fraction represents over half of the DOC present in the raw water. VHA and SHA DOC fractions are generally responsible for colouring raw water supplies and, along with the CHA fraction, contain compounds that are most likely to be removed by conventional treatment processes. Generally less than 10% of the NEU fraction can be removed using chemical coagulation. Between 40% and 60% of raw water DOC is generally removed when coagulation, flocculation and some form of separation process is used to produce drinking water, but this does depend on the character of the raw water source.

Other compounds that contribute to DOC generally do not contribute to visible colour in water and the chemical coagulation process does not significantly affect them so they can be considered as recalcitrant fractions. These compounds in combination with the remaining DOC fractions after treatment become precursors to DBP formation as well as food for biofilm production and they exert a disinfection demand.

Membranes offer another tool to designers and operators to reduce DOC by up to 90% or more compared to conventional processes that can remove between 40% and 60% depending on the quality of the raw water. Increased DOC removal will certainly reduce disinfectant demand, DBP formation and also significantly limit the growth of biofilms in the distribution network.

## 3.0 NANOFILTRATION AND ULTRAFILTRATION MEMBRANES

The evolution of membranes has created an opportunity to meet the needs of our customers by eliminating chemicals used for coagulation and at the same time provides better water quality. The advent of nanofiltration (NF) and 'tight' ultrafiltration (UF) membranes provides water authorities with a new set of tools to remove more than just the DOC that produces coloured compounds from soft water without the need to chemically treat the water. NF and UF membranes also provide a significant improvement as a barrier against bacteria and viruses. UF and NF membranes are capable of removing microbial and viral contamination that is several orders of magnitude greater than 'conventional' water treatment processes such as dissolved air flotation and filtration (DAFF). The improved barrier to the passage of microbiological and viral contamination reduces the risk of disease transmission.

Using UF or NF membranes will significantly reduce NOM, the precursor to DBP production, and has the potential to reduce the disinfectant dose rate necessary to maintain a residual concentration to protect consumers. These type of membranes also ensure that other contaminants such as turbidity are eliminated and do not have a detrimental effect on the water quality.

Removing a greater proportion of DOC from the water also serves to minimise the growth of biofilms in distribution networks by limiting the food available. Reduced biofilm growth provides better water quality and can reduce maintenance activities within the distribution system.

Chemical coagulation of coloured water supplies generates a significant quantity of mostly inorganic sludge that may pose a disposal problem. Aluminum and iron sludges can lock up soil phosphorus and make it unavailable to plants, so beneficial use is severely limited.
The potential to use the concentrated DOC rejected from the membrane process as a soil conditioner reverses the trend of disposal to one of beneficial reuse.

The footprint of a UF or NF process is significantly smaller than 'conventional' water treatment processes. A smaller footprint and no generation of metal salt sludges have the potential to overcome the development of sensitive sites. NF and UF membrane systems can be considered chemical free because they do not require metal salt addition to reduce NOM. However, a conventional disinfectant may be added and membrane-cleaning processes do require small amounts of chemicals to clean the membranes at varying frequency throughout the year. Consequently, there are many potential benefits associated with the use of UF or NF membranes in the reduction of NOM before disinfection.

UF and NF membranes are available as either spiral wound elements, tubular membrane elements with an integral swabbing mechanism or sintered ceramics among other materials. The following case studies review spiral wound and tubular membrane applications used to treat coloured water.

## 4.0 THE EXPERIENCE

The experience of meeting a number of researchers, treatment plant operators, membrane manufacturers and membrane system designers and integrators was invaluable. The knowledge shared by the people visited was considerable and included some valuable insights when things don't go according to plan. Some of their information is included in this presentation and the network that has been developed as a result of the Kwatye Prize is available to anyone in the water industry interested in this specific application of membranes.

### 4.1 *Irvine Ranch Water Treatment Plant*

Southern California is growing so quickly that a coastline about the same length as Melbourne to Portland currently is home to the entire population of Australia, more than 20 million people. This population growth has placed tremendous strain on the available water resources and alternative water sources are being developed to cater to the ever-increasing demand.

One of the water districts that serve communities south of Los Angeles is the Irvine Ranch Water District (IRWD). IRWD have developed a water resource from an unused aquifer approximately 670 m deep to provide water to their growing community. The water is very old and has a colour of around 200 HU with a temperature of $30^{0}$C and 15 mg/L of methane. Chemical coagulation was not a viable option, as the character of the water did not lend itself to efficient DOC and colour removal.

IRWD designed and installed a three-stage nanofiltration membrane system in 2002 using Hydranautics HydraCoRe thin film composite membranes. Methane stripping towers were also installed after the membrane process to ensure that the water was free of dissolved methane. It is interesting to note that a cogeneration system was considered to generate electricity from the captured methane but it was not considered financially viable.

Three tapered NF arrays each with a configuration of 36 pressure vessels in the first stage, 18 in the second stage and 7 in the third stage provided an average of 92% recovery.
Each pressure vessel is fitted with seven HydraCoRe thin film composite membranes so each array contains 427 elements and the three arrays have a total of 1,381 eight-inch NF membrane elements. The existing three stage arrays have the capacity to continuously deliver just over 30 ML/d.

Reject water from the plant is disposed to sewer, however the sewerage system belongs to another water authority and IRWD pay a trade waste disposal charge. The trade waste disposal charge prompted IRWD to design and install a fourth stage due for completion at the end of 2006. Incorporating the fourth stage will improve recovery to slightly more than 98%; this is a better recovery than most conventional water treatment processes, but it does come at a cost.

It is interesting to note that the NF membranes have had a clean in place (CIP) performed only once during the past four years of operation. This tends to indicate that this DOC does not support microbes because the fouling rate would be far greater if the DOC was readily degradable. The unusual anaerobic nature of this water source means that such performance cannot, in general, be expected.

### 4.2 *Scottish Water and the tubular Nanofilter from PCI*

Scottish Water is the new merged entity of three former water authorities that provides water and sewerage services to a population of 4.85 million people and covers an area approximately the same size as that covered by GWM Water, about 60,000 $km^2$. Scottish Water currently supplies water to over seventy communities using tubular nanofilters, and to a lesser degree spiral wound NF membranes. Raw water throughout the highlands of Scotland is soft, aggressive and coloured and is often subject to extreme fluctuations in colour that all of the operators visited described as ‘flashy’. Two important aspects that should be noted and they are that the colour may average 60-100 HU but when rain is experienced the colour of water in the lochs can become very coloured, similar to the dark tea coloured waters in western Tasmania and southern Victoria, and the water temperature often drops below $2^{0}$C.

Tubular nanofiltration systems in western Scotland at Ardfern (120m$^3$/d), Kilchrenan (750m$^3$/d), Inchlaggan (10m$^3$/d) and Glenuig (70m$^3$/d) were inspected with personnel from the membrane system supplier, PCI a subsidiary of ITT Flygt, and the duty Scottish Water operator. A larger spiral wound NF treatment plant at Kyle of Lochalsh (1,920m$^3$/d) on the mainland entry to the Isle of Skye provided an interesting comparison.

Scottish and Norwegian NF plants utilise cellulose acetate (CA) membrane materials rather than the polyamide thin film composite (TFC) material typically used in many of the NF plants in America and Méry-sur-Oise in northern Paris. One of the perceived benefits that CA membranes provide is the ability to dose chlorine before the membranes on a daily basis for about an hour to help control biological fouling of the membranes. TFC membranes cannot tolerate oxidants like chlorine but they can tolerate chloramines addition and this is sometimes used to help control biofouling.

Tubular membranes, supplied by PCI, are used at most of the smaller water treatment plants at places like Ardfern, Inchlaggan, Kilchrenan and Glenuig. The tubular NF membrane elements are like oversized straws that are 10mm in diameter and each element has 72 tubes that are 4 metres long providing just over 260 m$^2$ of membrane area.

PCI manufacture up to 30 different membrane materials from very tight UF to NF specifications.

The tubular membranes have a significant advantage over spiral wound elements because pretreating the water to remove turbidity is not required. Turbid water is allowed to enter the tubular membranes and particulate fouling is controlled by using a foam ball that swabs the membrane surface. The foam ball is slightly smaller than the internal diameter of the NF membrane and the passage of foam swab induces turbulence that assists in controlling particulate material blinding the membrane surface. The swabbing operation takes about eight minutes to complete and occurs every four hours of operation, although this frequency is adjustable. A recirculation stream is required to ensure that sufficient cross flow is maintained to help control fouling and maintain the desired recovery.

Operators at Kilchrenan WTP Kyle of Lochalsh WTP both agreed that the tubular NF treatment plants were generally easier to operate because the automated swabbing helped to control the fouling and the NF membranes consistently produced excellent water quality with a “minimum of fuss”.

Some of the tubular NF membrane operating parameters such as membrane flux was 24 L/m2.h at a recovery of between 65% and 75%. The raw water temperature at the time of the site visit at Inchlaggan was 6.2$^0$C, however the operator provided records that indicated the raw water temperature varied between 0.6$^0$C and up to a maximum of 12.2$^0$C. This extreme raw water temperature range certainly tests membrane processes but the Scottish experience shows that they can be employed to deliver excellent water quality even in the most trying of conditions.

Chlorine is used as the disinfectant of choice and is dosed into the filtered water at a rate of 0.25mg/L to 0.35mg/L to achieve a chlorine residual concentration of around 0.15mg/L at the end of the distribution network.

### 4.3 *The Norwegian experience*

Norwegian provincial councils own and operate water treatment plants, as is the case in NSW, Queensland and Tasmania. Nanofiltration processes are used to produce drinking water to over one hundred communities throughout Norway. The Orkdal Water Treatment Plant, just south of Trondheim, represents a typical treatment plant and uses spiral wound CA nanofiltration membranes that can deliver 8ML/d. The raw water temperature was $2^0$C and can climb up to $8^0$C during the warmer periods of the year.

The molecular weight of NOM in Norwegian waters is higher than that experienced in Australia and therefore the larger molecules are generally easier to remove. This specific feature of the raw water character provides an opportunity to use an NF membrane with a higher molecular weight cut off (MWCO) or alternatively, a 'tight' UF membrane may provide satisfactory performance.

The raw water supply contains 2.3mg/L of DOC, pH range of 7.1 – 7.5, colour of 25 HU, 50 mg/L Calcium as $CaCO_3$ and an EC of 80 µS/cm. A chlorine dose rate of 0.1mg/L is used to maintain a residual chlorine level of 0.05mg/L in the distribution network.

The Lello WTP provides drinking water to the community in and around the town of Levanger located about 100 km north of Trondheim.
The plant was originally designed to produce 10 ML/d but is currently only capable of producing 6 ML/d. The raw water supply contains 4.7mg/L of DOC, pH of 7.4, colour of 27 HU, 50 mg/L Calcium as $CaCO_3$ and an EC of 69 µS/cm. A chlorine dose rate of 0.15mg/L is used to maintain a residual chlorine level of 0.05mg/L in the distribution network.

A well-respected Norwegian contractor that had experience with membrane plants delivered the Lello WTP. Unfortunately the plant has not been able to deliver the required flow rate of 10ML/d and can only produce 6 ML/d with daily maintenance cleans and a clean in place (CIP) every two weeks. The process design and configuration were not optimised for the raw water quality at Levanger and was a copy of a similarly sized plant. Professor TorOve Leiknes from Trondheim University (NTNU) recommends properly characterizing the raw water and undertake some pilot trials using a variety of membranes and conditions to optimise the design before construction rather than just blue printing a similar design.

Most of the Norwegian nanofiltration treatment plants use cellulose acetate spiral wound membranes manufactured by Koch Membrane Systems, as is the case for Scotland.

### 4.4 *pH correction using Calcite*

The lightly buffered water is pH adjusted after nanofiltration and before it is delivered to the distribution network. Treated water pH is adjusted by passing the filtered water through a bed of granular calcite that is crushed dense limestone also known as marble. Once the soft water comes into contact with the calcite the material dissolves and provides a source of calcium hardness and bicarbonate alkalinity. The operator replaces the dissolved material whenever the recharge level is reached. This is a simple and very effective process and replaces alternatives such as lime dosing. GWM Water is currently building a new membrane treatment plant for the communities of Willaura and Lake Bolac using calcite and carbon dioxide to adjust pH and alkalinity in the finished water.

Calcite beds can also be used to remove iron and manganese from water by chlorinating the feed water. The iron and manganese is oxidised by the chlorine and forms complexes that deposit on to the calcite. Scottish Water experiences indicate that the removal efficiency of this type of process is extremely high.

## 5.0 CONCLUSION

It is clear that nanofiltration and to a limited extent 'tight' UF extend the range of tools that designers and operators of water treatment plants have at their disposal to deliver good quality drinking water. While there are currently no nanofiltration plants in use to produce drinking water in Australia there are a few plants in far north Queensland that use Koch Membrane Systems UF membranes to reduce DOC without the use of chemicals. Reports suggest that a 40% reduction in DOC concentration is consistently achieved.

The Kwatye Prize has provided an opportunity to answer some of the questions posed at the beginning of this study and this may be the catalyst for the implementation of nanofiltration system, more so than ultrafiltration, specifically targeted to produce drinking water. Clearly, the application of nanofiltration needs to be targeted to meet treated water quality criteria when raw water characteristics such as soft, aggressive and coloured raw water suggest its use.
The answers to some of the questions are very positive while some questions remain unanswered and require further research. Some of the things that have become clearer as a result of the study tour include:

1. Recovery rate ranging from 65% to 98% are possible for nanofiltration systems using different DOC sources. It is evident from the wide variety of raw water sources being treated overseas that raw water characteristics typical of those found in Tasmania, tropical north Queensland and the Northern Territory and the mountain regions of Victoria and NSW as well as parts of West Australia would be suitable candidates for treatment using NF.
2. Irvine Ranch WTP is evidence that recovery rates as high as 95% are possible but it is also clear that raw water characterisation and pilot scale testing are essential before implementation.
3. The effect that raw water temperature has on DOC removal is dependant on the raw water character but the water density will reduce and flux rates will increase as the water temperature increases.
4. Fouling is considered to be one the most important factors when considering the application of NF membranes and is an area that needs careful attention during the pilot scale testing, design and operation phases.
5. Increased fouling rates are expected as the raw water temperature increases and special attention is required to determine what strategies should be employed to minimise the effect of fouling. Scheduled pre-chlorination of the NF feed water using cellulose acetate membranes could be one such strategy.
6. The concentrated food source available on the reject side of the membranes will certainly promote biofouling because it was evident at most treatment plants visited even at temperatures below $5^{0}$C.
7. The limitations of water quality with respect to the types of DOC and alkalinity concentrations as well as calcium hardness are dependant on the design parameters such as flux rate, recovery and cross flow. Raw water characteristics such as calcium hardness and alkalinity may be limiting and may reduce the

likelihood of NF membrane applications.

8. The rejected concentrated DOC was returned to the source water and was not reused in any treatment facility visited. There appears to be no reason why the concentrated DOC cannot be used as a soil conditioner. The beneficial reuse of the concentrated DOC may still be viable where antiscalants are used to improve membrane performance to reduce fouling because antiscalant formulations may be suitable for such applications.

The focus on water quality will increase over time and alternative technological solutions will be required to meet the need. New products such as nanofiltration and ultrafiltration membranes have the capacity to reduce NOM, which is recognised as the significant precursor to the formation of DBP. Reducing DOC levels in drinking water will also maintain the improved water quality through the distribution network right up to the consumers tap and that is the sort of service we, as water industry professionals, need to provide.

## 6.0 ACKNOWLEDGEMENTS

This study tour would not have been possible, or even contemplated, without the financial support associated with the award of the Kwatye (Water) Prize.

I am very grateful to the Water Industry Operators Association (WIOA) and the sponsors of the Prize, Environmental & Process Technologies (Division of Biolab), for the opportunity to undertake the extensive study tour. I am also honoured to chosen as the inaugural recipient of the Kwatye (Water) Prize.

I would also like to thank Mr. Peter McManamon, CEO of GWM Water, for his immediate support and acknowledge the support and financial contribution to the study tour by GWM Water. I am sure that GWM Water will gain benefits from this study but their willingness to support the tour, and my continued absence for 5 weeks, was remarkable.

Finally, I would like to thank all the people who provided various overseas contacts during the planning phase of this study tour, particularly Mr. Gabriel Vigna of ITT Flygt Ltd who made the Scottish, Swedish and French legs of the trip memorable. Certainly my thanks go out to the eighty or so people that spent their time educating me in the finer points of membrane manufacture, design and operation.