Assessment of water treatment processes: detailed organic matter characterisation and membrane fouling indices at the Loddon Water Treatment Plant, Victoria, Australia

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ABSTRACT

Recent advances in membrane technology have led to its broad application, and reverse osmosis (RO) systems now represent the fastest growing segment of the desalination market. Its performance is hindered by membrane fouling. In this study pre-treatment methods to reduce RO fouling were investigated including flocculation, adsorption and ion exchange. Detailed organic characterisations were made in terms of florescence spectroscopy excitation emission matrix (EEM), UV\textsubscript{254} absorbance and liquid chromatography-organic carbon detection (LCOCD). The different pre-treatment methods were assessed in terms of the fouling potential. This was quantified in terms of the modified fouling index measured using a dead-end cell micro-filtration (MF) unit. The existing pre-treatment of granular activated carbon (GAC) filter led to a good organic removal. Among the pre-treatment methods tested in the laboratory, Purolite ion exchange/adsorption was found to be better than FeCl\textsubscript{3} flocculation in terms of the amount as well as the wide range of organics removal. A pre-treatment of flocculation with Poly-ferric-silicate (PFSi) as flocculent gave a higher removal of organic matter compared to other pre-treatments tested. DOC was reduced from 11.5 to 4.25 mg/L, and it removed mostly the humic type substances.

Key words | adsorption, biofilter, desalination, flocculation, fouling index, membrane process

INTRODUCTION

The growth in membrane applications for desalination has been exponential over the last decade and is expected to continue as the per capita water requirements increase. Recent advances in membrane technology have led to its broad application, and reverse osmosis (RO) systems now represent the fastest growing segment of the desalination market. Nevertheless, the operation of membrane-based desalination plants still remains complex mainly due to membrane fouling.

Membrane fouling is an extremely complex phenomenon which occurs by the formation of undesirable deposition of particulate/colloidal or organic matter on the membrane surfaces (Al-Amoudi & Lovitt 2007). The types of RO fouling can be classified on the basis of fouling materials: (1) particulate and colloidal matter fouling; (2) inorganic fouling due to deposition of inorganic scales (such as CaSO\textsubscript{4} CaCO\textsubscript{3}) on the membrane surface; (3) organic fouling due to organic material (OM) found in the process stream (e.g. humic acids, protein and carbohydrate); and (4) biofouling due to microbial attachment to membrane surface followed thereafter by their growth and multiplication in the presence of adequate supply of nutrients in the pre-treated feed or nutrients that deposited on membrane surfaces. Inorganic and particulate/colloidal fouling has been extensively studied and can be controlled efficiently. However, the quantification of organic fouling requires sophisticated methods and analytical tools to characterize soluble organic matter. Organic fouling is usually discussed in terms of adsorption of various dissolved organic materials on and in the membrane.
Both particulate/colloidal and organic fouling can be controlled by pre-treatment. As a result, effective pre-treatment of water can provide good quality feed water to RO desalination plants. Moreover, it will reduce the fouling of RO membranes and reduce the energy requirements.

This study evaluated the performance of different pre-treatment methods to RO in the Loddon Water Treatment Plant in Victoria, Australia, (Coliban Water 2011). The plant provides potable water to the towns of Bridgewater and Inglewood in Victoria. Raw water is drawn from the Loddon River at Bridgewater. Low river levels due to the ongoing drought in recent years have reduced the quality of raw water, including elevated salt levels and organic matter, entering the water treatment plant. The existing treatment plant was not able to remove the salt and the plant was recently augmented by a RO desalination plant housed in two shipping containers. Water is now treated using the existing water treatment facility, and then some of the water goes through the desalination process to reduce the salt levels. The blending of water ensures there is a right balance of minerals in the water supply and avoids the need to add anything further.

The objectives of this study were: (i) to characterise samples of raw water, effluent from the pre-treatment, RO effluent and RO concentrate from the Loddon water treatment plant in Victoria and to (ii) experimentally test other pre-treatment alternatives that could reduce RO fouling. Other pre-treatments tested were flocculation, adsorption and ion exchange. Detailed organic characterisations were made in terms of florescence spectroscopy excitation emission matrix (EEM), UV$_{254}$ absorbance and liquid chromatography-organic carbon detection (LC-OCDD). The different pre-treatment methods were also assessed in terms of the fouling potential. The reduction in membrane fouling was quantified by the fouling index as measured using a dead-end cell microfiltration (MF) unit.

**ANALYTICAL METHODS**

**Raw water**

Wastewater was collected from the Loddon water treatment plant in Victoria, Australia. Organics present after the pre-treatment were analysed in terms of organic removal.

**Fouling index**

A dead-end filtration unit was used to measure the modified fouling index (MFI). The MFI was measured using a dead-end cell using a 0.45 μm micro-filter (MF-MFI). New membranes were used in each experiment to avoid the effect of residual fouling and to compare the results obtained under different conditions in a consistent manner. Feed water into a flat sheet membrane module (diameter of 47 mm) was pressurized and the trans-membrane pressure (TMP) was controlled at 200 kPa by means of pressure regulating valve (Chinu et al. 2010).

The MFI is determined from the gradient of the general cake filtration equation at constant pressure by plotting $t/V$ versus $V$ using Equation (1)

$$
\frac{t}{V} = \frac{\eta R_m}{\Delta \text{P} A} + \frac{\eta \alpha C_b}{2 \Delta \text{P} A} V
$$

where $V = \text{total permeate volume (l)}$, $R_m = \text{membrane resistance}$, $t = \text{filtration time (s)}$, $\Delta \text{P} = \text{applied trans-membrane pressure (Pa)}$, $\eta = \text{water viscosity at 20 °C (N s/m²)}$, $\alpha = \text{the specific resistance of the cake deposited}$, $C_b = \text{the concentration of particles in a feed water (mg/L)}$, $A = \text{the membrane surface area (m²)}$.

MFI is defined as the gradient of the linear region of $t/V$ vs $V$ plot normalized to standard reference values of 207 ± 3 kPa transmembrane pressure, a feed water temperature of 20 °C and MF/UF with a surface area of 47 mm diameter.

**Liquid chromatography-organic carbon detection (LC-OCDD)**

Liquid chromatography-organic carbon detection (LCOCDD) was used to identify classes of organic compounds in the water samples before and after treatment. It gives quantitative information on natural organic matter (NOM) and qualitative results based on molecular size distribution of organic impurities in water. Quantification is realised by carbon mass determination, similar to total organic carbon (TOC) analysis, performed with a special organic carbon detector. The qualitative analysis is based on size exclusion chromatography (SEC). SEC separates components on the basis of their molecular size. Water samples are injected into a column filled with a chromatographic gel material. Substances with small molecular sizes can access more of the internal pore volume than those with larger sizes.
**UV$_{254}$**

The absorbance value at 254 nm was used for the estimation of non-specific parameters such as TOC. Ultraviolet (UV) spectroscopy has been widely used in monitoring water and wastewater treatment. James et al. (1985) suggested that UV absorbance at 254 nm was an excellent surrogate parameter for total organic carbon (TOC) and total trihalomethane (THM) formation potential. The absorbance value at 254 nm has been used for the estimation of non-specific parameters such as BOD and COD in water and wastewater. The choice of this wavelength was not due to scientific reasons but due to the widespread availability of cheap UV sources (low-pressure Hg lamps). Kalbitz et al. (2000) characterized dissolved organic matter, particularly fulvic acid, using UV spectroscopy. Chevalier et al. (2002) compared the use of the conventional standard method and the UV absorbance method to measure BOD$_5$ (5–115 mg/L) and TOC. Their results indicated that the measurement for BOD$_5$ was good, with a correlation coefficient ($R^2$) of 0.67, whereas TOC did not show a satisfactory correlation.

**EEM**

Fluorescent fingerprint or excitation emission matrix (EEM) has been widely used to identify the nature of organic substances in water and wastewater. The main advantage of EEM fluorescence spectroscopy is that information regarding the fluorescence characteristics can be acquired by changing the excitation wavelength and emission wavelength simultaneously without destroying the samples. More details on the nature of organics and the corresponding ranges of the excitation wavelength and emission wavelength can be found elsewhere (Chen et al. 2003; Aryal et al. 2009).

**RESULT AND DISCUSSIONS**

**With the existing pre-treatment at Loddon treatment plant**

The MF-MFI values of samples of the water collected following various treatment stages at the Loddon water treatment plant were measured and the results are summarised in Table 1.

The MF-MFI of raw water was 287 s/L$^2$. It reduced only marginally to 275 s/L$^2$ after a pre-treatment of filtration. It indicates any one of the following: that there was not much removal of micron size colloidal/suspended particles in the water, or these particles were not present in the water or these particles were not effectively removed by media filtration. This value significantly reduced to 25 s/L$^2$ after granular activated carbon (GAC) adsorption which was used as a second pre-treatment before RO. This indicated a majority of organic matter was removed by GAC filter.

UV$_{254}$ absorbance was measured for water samples before and after pre-treatment. The raw water had a UV$_{254}$ absorbance of 0.1914. The existing pre-treatment of GAC adsorption had a UV$_{254}$ absorbance of 0.11. It was found that filtration and GAC adsorption removed only 43% of the organic matter present in the raw water.

Fractionations of organic matter were also conducted in water samples collected following various treatment stages at the Loddon water treatment plant, Table 2. It was observed that DOC for raw water was 11.54 mg/L out of which only 3.5% of organics were hydrophobic and the remaining 96.5% organics were hydrophilic. Among hydrophilic substances, most of the organics present were humic type substances (43%) and the others were biopolymer (20.7%), building blocks (23.3%) and low molecular weight (LMW) neutrals (21.7%). With the existing pre-treatment at Loddon treatment plant, the combination of filtration and GAC adsorption reduced the DOC to 7.9 mg/L. This pre-treatment mainly removed large bio-polymer type of organic compounds.

<table>
<thead>
<tr>
<th>Sample</th>
<th>MF-MFI s/L$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw water</td>
<td>287</td>
</tr>
<tr>
<td>Water after filtration as a pre-treatment</td>
<td>275</td>
</tr>
<tr>
<td>Water after the pre-treatment of filtration and GAC adsorption (RO influent)</td>
<td>25</td>
</tr>
<tr>
<td>Effluent of RO</td>
<td>3</td>
</tr>
<tr>
<td>Concentrated reject water entering the brine tanks (RO concentrate)</td>
<td>300</td>
</tr>
</tbody>
</table>

Table 1 | MF-MFI and UF-MFI for influent, effluent and rejected brine of RO
Humic, building blocks and LMW type organic substances were also removed by the existing pre-treatment. The removals were about 40, 10 and 12% respectively.

Fluorescence spectral data (excitation emission matrix)

Figure 1 shows the EEM spectra of samples of raw water, after conventional filtration, after GAC filtration, after RO filtration and GAC adsorption pre-treatment.

Table 2 | Fractionation of OM by LC-OCD of water before and after existing pre-treatment in the plant

<table>
<thead>
<tr>
<th>Sample</th>
<th>DOC dissolved, mg/L, %DOC</th>
<th>HOC hydrophobic, mg/L, %DOC</th>
<th>CDOC hydrophilic, mg/L, %DOC</th>
<th>BIO-polymers, mg/L, %DOC</th>
<th>Humic substances, mg/L, %DOC</th>
<th>Building blocks, mg/L, %DOC</th>
<th>LMW neutrals, mg/L, %DOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw water</td>
<td>11.54, 100%</td>
<td>0.42, 4%</td>
<td>11.11, 96%</td>
<td>2.02, 18%</td>
<td>5.55, 48%</td>
<td>1.84, 16%</td>
<td>1.71, 15%</td>
</tr>
<tr>
<td>Effluent from pre-treatment</td>
<td>8.50, 100%</td>
<td>0.40, 5%</td>
<td>8.10, 95%</td>
<td>0.90, 11%</td>
<td>2.60, 31%</td>
<td>2.80, 33%</td>
<td>1.70, 20%</td>
</tr>
<tr>
<td>Influent to RO*</td>
<td>7.80, 100%</td>
<td>0.40, 5%</td>
<td>7.40, 95%</td>
<td>0.60, 8%</td>
<td>3.40, 44%</td>
<td>1.80, 23%</td>
<td>1.50, 19%</td>
</tr>
<tr>
<td>Effluent from RO</td>
<td>0.16, 100%</td>
<td>0.06, 58%</td>
<td>0.10, 65%</td>
<td>NQ</td>
<td>0.01, 6%</td>
<td>0.08, 50%</td>
<td>0.08, 50%</td>
</tr>
<tr>
<td>RO reject water</td>
<td>45.00, 100%</td>
<td>4.00, 9%</td>
<td>41.00, 91%</td>
<td>3.70, 8%</td>
<td>11.60, 26%</td>
<td>16.50, 37%</td>
<td>9.60, 21%</td>
</tr>
</tbody>
</table>

NQ – not quantified.
\*after filtration and GAC adsorption pre-treatment.

**Figure 1** EEM spectra of raw water, water after filter prior to GAC, influent to RO, effluent of RO and RO rejected brine.
filtration and the RO rejected brine. The LC-OCD and EEM data suggest that the conventional filtration does not remove any organic matter and some of the organics in the raw water are removed by GAC. The RO system removed almost all organics. However, EEM analysis of concentrated brine (RO rejected) shows a wide range of organics accumulated by RO. This shows that RO membranes will be affected in the long term and severe fouling may occur. Thus some additional pre-treatment will be useful to reduce fouling of RO membranes.

**Laboratory trials on alternative pre-treatment**

Removal of organics prior to RO is an important step towards sustainable RO operations, both in terms of technical and economic aspects. Two types of pre-treatment that help to remove organics from water were tested to minimise the fouling in RO. These were flocculation with FeCl₃ and poly ferric silicate (PFSi) and ion exchange with Purolite. 10 mg/L of FeCl₃ gave higher organic removal compared to 15 and 5 mg/L of FeCl₃. Purolite (0.5 g/L) removed a relatively higher amount of organic matter (34%). Flocculation with PFSi (at a dose of 3 mg/L) led to the highest organic removal among the pre-treatment methods studied.

The MF-MFI of the effluent after pre-treatment of flocculation with 10 mg/L of FeCl₃, 3 ml/L of PFSi, and ion/exchange and adsorption with purolite of 0.5 g/L were 270, 20 and 40 s/L² respectively.

Purolite adsorption with concentration of 0.1, 0.25 and 0.5 g/L gave rise to a lower UV₂₅⁴ absorbance value of 0.1235, 0.1006 and 0.0795 respectively. The raw water had a UV₂₅⁴ absorbance of 0.1914. On the other hand, the removal of organic matter was not significant when flocculation with FeCl₃ was used as a pre-treatment. The UV₂₅⁴ absorbance ranged from 0.1704, 0.1721 and 0.1764 for concentration of FeCl₃ of 15, 10 and 5 mg/L, respectively. Adsorption/ion exchange with purolite led to a relatively higher organic removal especially when a dose of 0.5 g/L was used (58%). PFSi also recovered 65% organics in terms of UV₂₅⁴.

Fractionations of organic matter were also conducted for water samples from different pre-treatments (Table 3).

It was observed that DOC for raw water was 11.54 mg/L out of which only 3.5% of organic matter was hydrophilic while the remaining 96% of organic was hydrophilic in nature. In hydrophilic substances, most of the organics present were humic type substances (43%) and others were biopolymer (20.7%), building blocks (23.3%) and low molecular weight (LMW) neutrals (21.7%). Different doses of FeCl₃ and purolite adsorption were used as pre-treatment alternatives. DOC was reduced to 7.6 mg/L after 0.5 mg/L purolite adsorption where this pre-treatment mainly removed large bio-polymer, humics, building blocks and LMW type organic substances. Compared to FeCl₃ flocculation, purolite adsorption removal efficiency was high.

Poly-ferric-silicate (PFSi) with a Si/Fe ratio of 0.5 and at a dose of 3 ml/L gave rise to higher removal of organic matter compared to FeCl₃ as flocculent. DOC was reduced to 4.25 mg/L. It removed mostly humic types substances.

<table>
<thead>
<tr>
<th>Sample</th>
<th>DOC dissolved mg/L</th>
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<th>CDOM hydrophilic DOC</th>
<th>BIO-polymers mg/L</th>
<th>Humic substances (HS) mg/L</th>
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<td>5.55, 48%</td>
<td>1.84, 16%</td>
<td>1.71, 15%</td>
</tr>
<tr>
<td>After flocculation (15 mg/L FeCl₃)</td>
<td>10.60, 100%</td>
<td>0.40, 4%</td>
<td>10.20, 93.1%</td>
<td>1.90, 18.2%</td>
<td>2.70, 25%</td>
<td>3.40, 32%</td>
<td>1.90, 18%</td>
</tr>
<tr>
<td>After flocculation (10 mg/L FeCl₃)</td>
<td>10.60, 100%</td>
<td>0.40, 4%</td>
<td>10.00, 94%</td>
<td>1.70, 16%</td>
<td>5.10, 48%</td>
<td>1.80, 17%</td>
<td>1.60, 15%</td>
</tr>
<tr>
<td>After flocculation (5 mg/L FeCl₃)</td>
<td>10.90, 100%</td>
<td>0.40, 4%</td>
<td>10.50, 96%</td>
<td>1.90, 17%</td>
<td>4.70, 43%</td>
<td>2.30, 21%</td>
<td>1.70, 16%</td>
</tr>
<tr>
<td>After purolite (0.5 g/L)</td>
<td>7.20, 100%</td>
<td>0.40, 6%</td>
<td>6.80, 94%</td>
<td>0.02, 0%</td>
<td>1.40, 19%</td>
<td>3.90, 54%</td>
<td>1.30, 18%</td>
</tr>
<tr>
<td>After purolite (0.25 g/L)</td>
<td>8.60, 100%</td>
<td>0.40, 5%</td>
<td>8.20, 95%</td>
<td>2.00, 23%</td>
<td>2.80, 33%</td>
<td>1.80, 21%</td>
<td>1.40, 16%</td>
</tr>
<tr>
<td>After purolite (0.1 g/L)</td>
<td>9.80, 100%</td>
<td>0.30, 3%</td>
<td>9.50, 97%</td>
<td>2.00, 20%</td>
<td>3.20, 33%</td>
<td>1.60, 16%</td>
<td>1.60, 16%</td>
</tr>
<tr>
<td>After flocculation with PFSi (3 ml/L)</td>
<td>4.25, 100%</td>
<td>0.30, 7%</td>
<td>3.95, 93%</td>
<td>0.21, 5%</td>
<td>0.47, 11%</td>
<td>1.40, 33%</td>
<td>1.26, 30%</td>
</tr>
</tbody>
</table>
Fluorescence spectral data (excitation emission matrix)

EEM spectra of raw and pre-treated water after FeCl₃ flocculation were measured and a comparison showed that there was negligible removal of organics by FeCl₃ flocculation.

Different doses of purolite ion exchanger/adsorption as a pre-treatment were applied for removal of organic substances. Figure 2 shows the EEM spectra of raw water and pre-treated water after purolite treatment. The EEM spectra showed a significant decrease in dissolved organics matter with larger doses of purolite. This shows that purolite is effective as a pre-treatment. Again to express this quantitatively, two major regions namely humic and fulvic type substances (Ex:Em 325/420 and 250/420 nm) were selected and the intensity correlated with the purolite dose. The spectra of pre-treated water by PFSi were similar to that of the purolite 0.5 g/L.

CONCLUSION

The existing deep bed filter as pre-treatment did not contribute much towards fouling reduction. However the GAC adsorption removed the organics to some extent and reduced the fouling considerably, according to the fouling indices results and dissolved organic carbon concentration reduction. Among the pre-treatment methods tested in the laboratory, purolite ion exchange/adsorption was found to be better than FeCl₃ flocculation in terms of the amount as well as the wide range of organics removal. On the other hand flocculation of PSFi led to the highest organic removal. Organic characterisation using LC-OCD was useful in identifying the suitable pre-treatment along with the MFI-MF values.

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