Demonstrating ultra-filtration and reverse osmosis performance using size exclusion chromatography

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ABSTRACT

Advanced water treatment plants employing ultrafiltration (UF) and reverse osmosis (RO) membrane processes are frequently implemented for the production of high-quality recycled water. It is important that process performance is able to be quantified and assessed to ensure it is fit for purpose. This research utilizes size exclusion chromatography with organic carbon, organic nitrogen and UV254 detection to determine the change in both DOC concentration and character through a UF/3 stage-RO pilot plant. It was determined that 97% of the influent DOC was removed on average to produce a water of less than 0.5 mg L\(^{-1}\) as C. The UF process removed more than half of the biopolymer fraction, equating to 4.5% DOC removal, while the RO process generally removed all DOC except a small proportion of the low MW humics and acids and low MW neutral fraction. While not changing significantly in concentration, the Stage 3 RO permeate typically contained low concentrations of humic fraction, indicating a change in character and therefore a change in rejection mechanism. Overall, it was determined that while TOC monitoring is important in advanced water treatment systems, improved understanding of the character of the TOC present lends greater insight into the assessment of process performance.

Key words | LC-OCD, organic carbon, reverse osmosis, ultra-filtration, water reuse

INTRODUCTION

Recent water shortages across Australia have instigated the testing of advanced water treatment plants comprising ultra-filtration (UF) and reverse osmosis (RO) membrane systems for the treatment of secondary treated effluent to a quality suitable for recharge of waterways or aquifers that might be used as a drinking water source (Wintgens et al. 2005). A challenge in implementing such water reuse systems is ensuring minimal risk to public health and therefore that treatment processes will be able to treat influent water to an acceptable level.

A key performance criterion in membrane treatment of secondary effluent is the removal of total organic carbon (TOC) component of the water. TOC comprises a multitude of different compounds, including (a) microbially derived proteins and carbohydrates, (b) refractory natural organic matter (NOM) which include humic and fulvic acids which may be present from stormwater or remain from drinking water, and (c) synthetic molecules including detergents, pharmaceuticals, and endocrine disrupting compounds and disinfection by-products (Shon et al. 2006). The latter group in particular are a potential health concern (Huerta-Fontela & Ventura 2008) and residual concentrations therefore need to be effectively controlled. TOC is therefore frequently monitored on-line to give an indication of process performance (Adham et al. 1998), and has been shown to be more important than conductivity measurements for RO systems (Kitis et al. 2003). However, TOC constituents are of variable character in terms of their molecular size, hydrophobicity and charge and therefore may not be removed to the same degree.
during treatment. Furthermore, some organic constituents are responsible for fouling membranes that are frequently utilized in the advanced treatment of wastewater (Jarusuthirak et al. 2002; Haberkamp et al. 2008). It is therefore important to understand the organic character of the water that will be treated by the advanced water treatment plant in order to make informed decisions regarding process operation.

One method that has been found to be useful for characterizing TOC composition is size exclusion chromatography (SEC), particularly when using organic carbon, UV absorbance at 254 nm (UV254) and organic nitrogen detection (Huber 1998; Jarusuthirak et al. 2002; Haberkamp et al. 2008, Her et al. 2008). The SEC technique separates organic matter predominantly according to size. For example, large molecules cannot permeate into the pores of the resin packing in the column and are thus eluted first. Smaller compounds are thereafter eluted generally in order of decreasing size. It is of note that other compound specific functionality including charge and hydrophobicity can initiate additional column interactions such that a very strict separation according to molecular weight cannot be stated. Nonetheless, previous research has identified typical wastewater fractions as “biopolymers”, “humics”, “building blocks”, “low molecular weight (MW) humics and acids” and low MW neutrals (Huber 1998; Her et al. 2002). Biopolymers comprise predominantly carbohydrates and proteins and elute near the “void volume” of the column which is the interstitial volume between the resin beads. The low MW humics and acids, for example carboxylic acids, elute immediately before the “permeation volume” of the column which is the sum of the interstitial and resin pore volume. Comparison with standards have shown that biopolymers, humics, building blocks and low MW humics, acids and neutrals have approximate MWs of >20,000 g mol\(^{-1}\), 1,000 g mol\(^{-1}\), 300–500 g mol\(^{-1}\) and <350 g mol\(^{-1}\), respectively. Low MW neutrals are eluted after the permeation volume as a result of interaction with the column resin. In measuring the UV signal the specific UV absorbance (SUVA) of the entire sample is determined as well as the quantification of the proportion of low MW humic and acid fraction that is attributable to low MW humics and the overall aromaticity of the humic fraction. The nitrogen signal allows quantification of the proportion of biopolymers that are proteins, in addition to identifying the nitrogen ratio in the other peaks, and the presence of ammonia, urea and nitrate. It should be noted that while most organic nitrogen compounds have high oxidation yields, triazines and some N-heterocyclic compounds are exceptions, the latter of which has oxidation yields between 60–90%.

This paper describes the use of the SEC method to assess the performance of a pilot plant implementing ultra-filtration and reverse osmosis technologies for the production of high-quality recycled water.

MATERIALS AND METHODS

Pilot plant samples

An Advanced Water Treatment pilot plant comprising ultra-filtration (UF) unit, a balance tank of hydraulic retention time of 1.5 hours, and 3-stage reverse osmosis (RO) unit finishing with chlorination was used in this study (Figure 1). The 3-stage RO system has an 84% recovery, where 47, 25 and 12% are recovered from Stages 1, 2 and 3 respectively. Grab samples were obtained at eight time points over a 1 month period (88 samples in total) from 11 locations within the pilot plant, including the UF feed (tertiary treated effluent), UF permeate, RO feed, Stage 1, 2 and 3 RO permeates and concentrates, combined RO permeate and final effluent.
Size exclusion chromatography analyses

A DOC-Labor LC-OCD Model 8 (Germany) was utilised for the SEC analyses which has organic carbon, organic nitrogen and UV254 detectors. A Toyopearl TSK HW-50S column was used that has a particle size of 30 μm, length of 250 mm and internal diameter of 20 mm. The mobile phase employed was phosphate buffer at pH 6.37 (2.5 g L⁻¹ KH₂PO₄ and 1.5 g L⁻¹ Na₂(HPO₄)₂·H₂O) at a flow rate of 1.1 mL min⁻¹. An injection volume of 1,000 μL was utilised for UF feed and permeate and RO feed, while 3,000 μL of the RO permeates were injected. Concentrates required a five times dilution prior to analysis. The system was calibrated for (1) molar masses of humics using IHSS Humic acid and IHSS Fulvic acid, (2) total organic carbon using potassium hydrogen phthalate, and (3) total organic nitrogen using potassium nitrate. This system enables a total organic carbon and SUVA of the overall sample prior to separation by diverting a small proportion (5%) of the flow directly to the detectors, generating a signal response at approximately minutes. An in-line 0.45 μm filter was positioned in front of the column and detectors such that all organic carbon concentrations reported refer to dissolved organic carbon (DOC). The measuring range of this instrument is 10 to 5,000 μg L⁻¹ as C (compound-specific) allowing quantification of the DOC concentration and character for both UF and RO treated water. Software provided by DOC-Labor for the quantification of organic matter fractions was utilised.

RESULTS AND DISCUSSION

Influent dissolved organic matter character

The DOC influent to the plant was relatively stable, averaging 8.17 ± 0.5 mg L⁻¹ for the eight grab samples. Other water quality parameters recorded included pH, which ranged between 6.9–7.2 for the duration of the sampling, conductivity at between 815 and 940 μS cm⁻¹ and turbidity at between 0.1–0.3 NTU. Figure 2 illustrates a typical chromatograph of organic carbon, organic nitrogen and UV₂₅₄ traces for the tertiary treated effluent feeding the advanced water treatment works. It shows distinct biopolymer, humics, building blocks and low MW humics and acids peaks, with residual low MW neutrals and is typical of tertiary treated effluent (Drewes et al. 2005). On average, the biopolymer proportion was 4.2 ± 0.9%, of which approximately 37.8 ± 2.6% was proteinaceous. This is consistent with previous observations where secondary treated effluent was observed to comprise 4% biopolymers (Haberkamp et al. 2008). Total humics (humics plus low MW humics) represented 32.3 ± 3% of the UF feed DOC, while building blocks comprised 21.9 ± 2.4%. Low MW acids were found to be negligible since the majority of organic carbon in this fraction is attributable to low MW humics, while low MW neutrals comprised 23.8 ± 1.7% on average.

Treatment performance

On undergoing membrane treatment the concentration and character of the DOC altered considerably. Overall, the average DOC decreased only marginally over the UF process (4.5%), decreasing by a further 12.8% across the balance tank (Figure 3). The greatest decrease in DOC concentration of 96% was observed over the RO system, where the residual DOC concentration in the combined RO permeate was 0.3 ± 0.17 mg L⁻¹ (Figure 3). On chlorination this residual remained low at 0.5 ± 0.26 mg L⁻¹ for the time period. The changes in organic carbon throughout the treatment process are discussed for each unit operation.

Ultra-filtration

The majority of the DOC was of a molecular weight below that of the UF membrane nominal molecular weight cut-off,
which was 100 kDa (0.02 μm pore size), and therefore passed through the UF membrane, accounting for the very low DOC removal observed. As the UF process is primarily a barrier against particulate material, including viruses, as opposed to dissolved organics this is to be expected. Examination of the differential plot of the UF permeate chromatograph subtracted from the UF feed chromatograph (Figure 4) indicate that it is almost exclusively the biopolymer fraction that is removed which decreased by approximately 56.8 ± 4.7% on average. Other minor peaks at less than 0.2 relative signal response are attributed to experimental error. The biopolymer fraction is known to comprise high MW proteins and polysaccharides and it is of note that the proportion of protein contained in the UF feed (37.8 ± 2.5%) was comparable with that observed in the UF permeate (37.5 ± 1.7%), indicating that neither proteins nor polysaccharides were removed preferentially. Previous studies have shown that the biopolymer fraction is most likely to foul the membrane (Haberkamp et al. 2008; Zheng et al. 2009) and there is an indication that proteins in particular may be of importance in this respect.

**Balance tank**

A distinct and unexpected decrease in DOC of 12.8% was observed across the balance tank, where a decrease in concentration of 13, 12 and 7% was observed on average for the residual biopolymers, humics (sum of high and low MW) and building block fractions respectively. Figure 5 shows the differential plot of organic carbon for the UF feed and permeate.
permeate and RO feed chromatographs, demonstrating that of the humics it was the low MW, more assimilable, organic carbon rather than the high MW material that was predominantly removed, suggesting that microbial degradation could be responsible. The balance tank was black and positioned in sun-light and therefore increased temperature within the tank was anticipated, which could have increased the microbial activity. Increased temperature has previously been shown to enhance mineralization of bulk (Gruenheid et al. 2008). It is possible that the chemical addition may also have impacted on DOC but it was not possible to sample prior to chemical addition, therefore the impact is unknown.

**RO system**

A 95% decrease in DOC concentration was observed across the RO system (between RO feed and the combined RO permeate. This is comparable with that previously reported where three tertiary effluent treated by nano-filtration (NF)/RO achieved 94–96.4% removal with residual DOC concentrations of 0.18–0.28 mg L$^{-1}$ (Drewes et al. 2003). The DOC concentrations of the permeates of the individual stages did not differ significantly at 0.51 ± 0.2 mg L$^{-1}$, 0.37 ± 0.21 mg L$^{-1}$ and 0.4 ± 0.14 mg L$^{-1}$ for Stage 1, 2 and 3 permeates respectively. However, the concentrates for the same stages approximately doubled with each successive stage, resulting in average concentrations of 13.9 ± 1.0 mg L$^{-1}$, 27.0 ± 2.0 mg L$^{-1}$ and 51.1 ± 2.9 mg L$^{-1}$ respectively. This indicates that the permeate DOC concentration was not impacted greatly by the increasing concentration of the influent stream. However, although the concentration did not differ significantly, analysis of the chromatographs demonstrated that the character of the water quality did alter with successive stages (Figure 6). For Stage 1 only the low MW humic and acids fraction and low MW neutral was observed, while for Stage 2, a small proportion of the building block fraction permeated the membrane and by Stage 3 a low concentration of DOC from the humic fraction (0.1 mg L$^{-1}$) was observed. This illustrates that as the influent DOC concentration increased, while only a very slight increase in concentration was observed, a change in the character of the DOC permeating the membrane was apparent. The average molecular weight of the humic fraction that was found in the Stage 3 RO permeate was 511 ± 20 g mol$^{-1}$, much less than that of the humic fraction observed pre-RO at 657 ± 56 g mol$^{-1}$, indicating that large humic material was still effectively rejected. The permeation of a proportion of the humic fraction suggests that fundamental rejection mechanisms, such as electrostatic repulsion, may be challenged at very high influent DOC concentrations. However, the Stage 3 permeate only contributed 14% of the total combined RO permeate and therefore upon mixing with Stage 1 and 2 permeate, the resultant building block and humic substance concentrations were below the level of detection and not observable (Figure 6) (Gruenheid et al. 2008).

Interestingly, the concentration of the humic fraction present in the Stage 3 RO permeate decreased over the duration of the sampling period until by the final sampling event on the 11th December no humics were detectable (Figure 7).
There was no observable or quantifiable difference between the final product which had undergone chlorination and the combined RO permeate with respect to DOC concentration and character.

CONCLUSIONS

By monitoring the DOC concentration and character using LC-OCD, the performance of the advanced water treatment plant was able to be quantified and was found to effectively remove almost all the DOC present. A DOC removal efficiency of approximately 97%, producing a DOC concentration of less than 0.5 mg L\(^{-1}\), was observed. The UF process removed the biopolymer fraction, indicating the potential for membrane fouling, while generally only the very low MW fractions (less than \(<350\) g mol\(^{-1}\)) permeated the RO membranes. Stage 3 RO permeates were observed to contain concentrations of the humic fraction; however, on mixing with the Stage 1 and 2 permeates these concentrations fell to below the limit of detection and the humic fraction concentration decreased with time.

This research demonstrates that while monitoring TOC concentration on-line is clearly important, with increases indicating membrane underperformance or significant change to influent water quality, it is also important to have an understanding of the character of the organic matter. A change in character might be missed by bulk TOC measurements and this change could indicate that rejection mechanisms were compromised. Further research should focus on on-line, sensitive measurements indicating TOC character. For example, a recent review highlighted the potential benefits of utilising fluorescence spectroscopy as an on-line monitoring tool in membrane processes (Henderson et al. 2009). A combination of monitoring systems, for example fluorescence with TOC, would best reveal changes in chemical composition of the organic molecules, overcoming the limitations associated with a single monitoring technique.

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REFERENCES


