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Ozone enhanced ceramic membrane filtration for wastewater recycling

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Abstract

The Water Corporation of Western Australia uses polymeric ultrafiltration (UF) membranes across a range of applications including surface waters with high natural organic matter (NOM), recycling of secondary treated wastewater and pre-treatment for seawater reverse osmosis (SWRO). These challenging raw water conditions require expensive chemical dosing and clean-in-place (CIP) regimes, high frequency of membrane replacement and reduced membrane life. The greater durability of ceramic membranes, with optimal ozone and coagulant dosing, offer a potential capital and operating advantage over polymeric UF membranes. The Water Corporation collaborated with PWN Technologies (PWNT) to establish a ceramic membrane pilot plant at the Beenyup Wastewater Treatment Plant (WWTP). Optimised performance of the pilot plant was established and compared with existing UF membranes treating secondary treated wastewater prior to reverse osmosis (RO) in an indirect potable wastewater recycling application. Findings show a sustainable flux rate of 150 L/m^2/h is achievable with ceramic MF membranes while filtering secondary treated wastewater. Higher flux rates up to 250 L/m^2/h have been tested and are possibly sustainable, however, other bottlenecks in the pilot plant (ozone generator capacity) prevented longer test runs at this flux. Comparable design flux rates for polymeric UF membranes are 50 L/m^2/h.

Key words: ceramic, filtration, membrane, ozone, recycling, wastewater

INTRODUCTION

This article documents the methods and results of pilot testing work undertaken by the Water Corporation to explore the use of ceramic microfiltration (MF) membranes as an alternative to polymeric membranes for filtration of secondary treated wastewater prior to treatment by RO. The specific application investigated was at the Beenyup WWTP in Western Australia. The Water Corporation currently operates a full scale advanced water recycling plant at this site that treats the secondary effluent using polymeric UF membranes, RO and UV disinfection. Thus, the operation and performance of the ceramic MF process could be directly compared with the polymeric membranes in the full scale plant. The Water Corporation's primary interests for this trial were:

- To optimise the ceramic membrane operation on Beenyup WWTP secondary effluent.
- To obtain information to compare capital and operating cost of a full scale ceramic membrane filtration process unit in comparison to a polymeric membrane filtration process unit, including all associated chemical systems and plant ancillaries.
- To determine filtered water quality and pathogen removal levels for the ceramic membrane process.

- To determine other operational advantages and disadvantages of the ceramic membrane filtration process in comparison to the equivalent polymeric membrane system.

Water high in organics (e.g. freshwater NOM or wastewater chemical oxygen demand [COD]) and/or high suspended solids can present challenging conditions for polymeric UF membranes. Along with the CIP chemicals often used to manage biofouling, UF membranes used to treat such challenging water can be expensive to build (i.e. low flux, low recovery and large footprint) and expensive to operate (i.e. high CIP regimes and membrane replacement frequency).

Ceramic membranes are of interest due to their durability against CIP chemicals and their ability to operate at a high sustainable flux with higher recovery, smaller footprint and longer membrane life. Optimising coagulation and pre-ozone dosing is critical to establishing sustainable and cost effective ceramic membrane treatment against UF alternatives.

The Water Corporation have an established track record of applying UF membranes to treat high NOM surface waters, secondary treated wastewater for recycling and pre-RO treatment of seawater for desalination. In all these applications ceramic membranes have the potential to substantially reduce operating costs at equal or lower capital costs. To establish whether such improved performance can be achieved, the Water Corporation collaborated with PWNT to refurbish a ceramic membrane pilot plant and trial it at the Beenyup Wastewater Treatment Plant (WWTP) treating secondary treated wastewater. Engineering design and refurbishment of the pilot plant was undertaken through 2015–2016 and commissioning began in early 2017. Testing continued on through 2017 and into 2018.

In general, the approach for the pilot testing has been to optimise the pre-treatment (comprising coagulation/flocculation, pH adjustment and ozone dosing), backwash regimes and critical flux rates. This is generally achieved by individual test runs, with changes made to operational settings after each test run. Over time, the optimised conditions are realised, and the plant can then be operated over a longer time period (weeks to months, depending on how the optimisation tests have progressed) to observe how the process functions over time. The performance of the ceramic membranes, compared with UF membranes (which are treating the same wastewater prior to RO as part of an existing indirect potable wastewater recycling scheme), will also be assessed.

EQUIPMENT

The pilot plant includes a single element 25 m^2 Metawater ceramic MF membrane module with a feed pump capacity up to 10 m^3/h, allowing flux rates up to 400 $L/m^2/h$ to be trialled. Figure 1 shows a schematic of the ceramic MF pilot plant. All equipment including membrane, chemicals and ancillaries are housed in a single shipping container to allow deployment to other sites as required. The pilot plant was designed to provide the operational flexibility needed for research, including testing varying flux, ozone and coagulant doses, varying feed pH, contact time in flocculating tank and varying backwash and chemical enhanced backwash regimes. Sampling ports are located along the treatment train from inlet to outlet. Ozone is dosed into the feed water prior to a degassing tower to vent undissolved ozone. The ozone generator used is a WEDECO GSO 30 oxygen fed unit capable of producing 100 g/hr of ozone. Poly-aluminium chloride (PACl) is dosed following the ozone addition with the use of a static mixer and flocculation tank. PACl was chosen due to its wide use by the Water Corporation and previous experience in Singapore (Clement *et al.* 2016) suggesting it performs better than ferric chloride. Other chemicals available for pH correction, enhanced backwash and CIP included sodium hypochlorite, hydrochloric acid and sodium hydroxide.

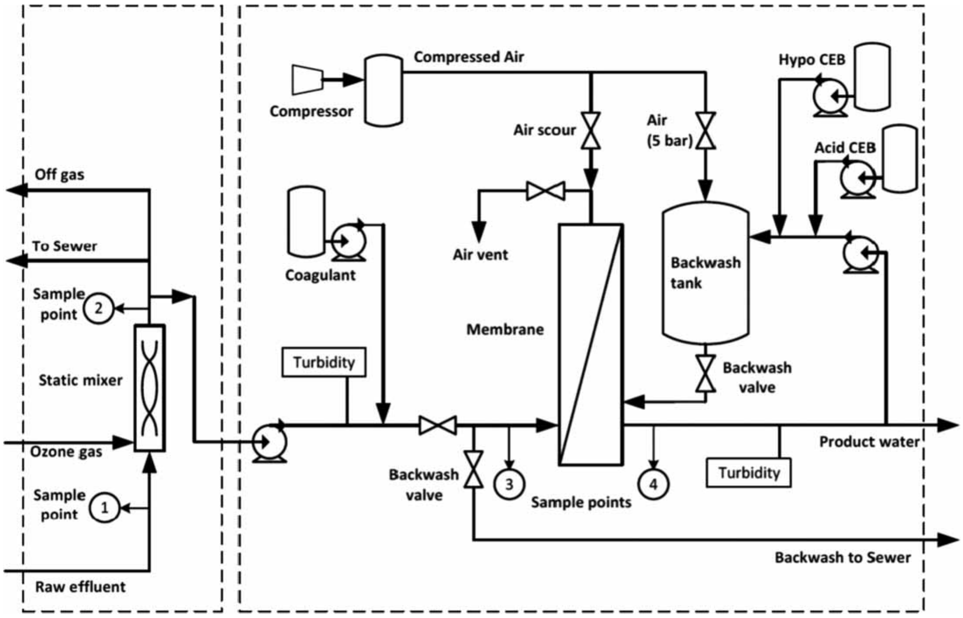

Figure 1 | Schematic of pilot plant.

METHODS

Analytical methods and measurements

Analytical methods used during execution of the study included the following:

- Ultra-violet transmissivity (UVT_{254}) – Hach direct measurement method 10243
- pH – measured by either inline or handheld amperometric sensors with temperature compensation
- Total/dissolved organic carbon (TOC/DOC) – by combustion TOC (5310-B)
- Transmembrane pressure (TMP) – direct online measurement by pressure transmitters located immediately upstream and downstream of the membrane pressure vessel
- Temperature compensated flux (as used to determine temperature compensated membrane permeability) (Allgeiers 2005).

$$J_{20} = J_T \cdot [1.784 - (0.0575 \cdot T) + (0.001 \cdot T^2) - (10^{-5} \cdot T^3)]$$

where

J_{20} = normalized flux at 20 °C (L/m^2·h [gpd/sq ft]),
J_T = actual flux at temperature T (L/m^2·h [gpd/sq ft])

Pre-treatment, backwash and CIP regime

Pre-treatment for the ceramic microfilter includes coagulant dose, pH control and ozone dose. Coagulant dose settings are made after jar testing to identify the optimum for organics reduction (measured as UVT_{254} increase). Through much of the study thus far a constant coagulant dose was used, however, there were also some trials to observe the influence of higher and lower coagulant dose.

Initial assessment of ozone demand suggested that about 16 mg/l would be needed to achieve an ozone residual on the membrane of about 1.0 mg/l. Previous work by PWNT and Duke (2014) showed that a residual of >0.8 mg/L allowed for sustained, high-flux operation when treating water and secondary effluent wastewater.

Initial operating criteria for coagulation and ozone dosing was thus established as follows:

- A PACl dose of 6 ppm as Al^{3+}
- A target ozone dose of 0.9 mg/L at the inlet to the membrane
- Coagulation pH was not adjusted, operating at the feed wastewater pH between 6.4 and 6.8

The pilot plant was also configured to allow maintenance of membrane performance through a number of backwash and CIP regimes as described below:

- Backwash (BW)
  - Conventional reverse flow backwash
- Enhanced backwash (EBW)
  - Type EBW-A

    Conventional BW enhanced by the addition of 100 mg/L sodium hypochlorite with 10 minutes' membrane soaking
  - Type EBW-B

    Conventional BW enhanced by the addition of a hydrochloric acid (pH ~ 2) with 10 minutes' membrane soaking
- CIP chemical cleansing
  - Traditional CIP

    Typically filtrate with 500 mg/l chlorine followed by an acid clean at pH 2 to 3
  - Ozone CIP

    Typically filtrate with >6 mg/l ozone, recirculated for about two hours

Typically several backwashes are undertaken before an enhanced backwash is applied. Further, a number of enhanced backwashes are completed before a CIP is applied. This is typically described in a backwash sequence such as 9 BW : 4 EBW-A : 1 EBW-B, which implies 9 BWs are undertaken before an EBW type A is completed. After 4 EBW type A a EBW type B is applied. CIP (usually the ozone CIP) was only applied when seeking to restore the ceramic membrane back to as new condition for the start of a new series of tests.

Optimisation objectives

The objectives of the trial are to establish and optimize operational parameters for the plant as follows:

- Establish a suitable ozone concentration at the membrane
- Establish a suitable coagulation dose and flocculation regime
- Determine the impact of varying feed pH on ozone and membrane performance
- Understand the impact of EBWs and establish optimum BW regimes
- Establish optimal flux.

Performance assessment

The membrane operational performance was evaluated based on the following operating criteria:

- Average transmembrane pressure (TMP) in kPa with temperature corrected to 20 °C
- Average permeability in l/m^2 h.bar with temperature corrected to 20 °C
- Overall fouling rate in normalised TMP increase per day (kPa/day at 20 °C) and derived CIP frequency

Filtrate water quality with respect to TOC, DOC, UVT_{254} and residual coagulant has been undertaken, but will not be reported here. Achievement of the desired test duration or high TMP (which was occasionally caused by deteriorating feed water quality) determined the end points of the various optimisation tests undertaken. Typically, filtrate water quality was very good at 0.01–0.05 NTU.

Experimental test plan

A series of test 'runs' were undertaken to determine the operating criteria for critical flux, BW frequency, enhanced BW frequency and longer-term stable operation. The following outlines the test runs undertaken:

- Testing the effect of ozone pre-treatment
- Testing increasing fluxes at set ozone and coagulant concentrations
- Testing varying feed pH on ozone and membrane performance
- Testing varying PACl dose at set ozone concentrations and flux
- Testing the effect of enhanced BW frequencies

As a starting point for the optimization work on Beenyup secondary effluent, the operating parameters determined in other studies contained in Clement *et al.* (2016) and Duke (2014) were used as a guide. The laboratory testing, showing an ozone demand of 16 mg/L was used to set the initial pilot plant ozone dose. From these starting values sensitivity test runs were conducted for each major operating variable, adjusting the setting for that variable both up and down while holding other parameters as constant as practical. Each test run would typically be operated from one day up to one week in order to determine whether the operating condition was sustainable (i.e. constant long-term permeability achieved) or unsustainable (i.e. decreasing long-term permeability observed).

By methodically working through each major operating variable over many tests, an optimal set of operating parameters was converged upon.

Long-term stable operation

The remaining weeks of pilot testing are planned to be stable operation of the ceramic membrane system. The goal is to show that the operation of this system at the determined optimum design parameters (i.e. flux, BW and EBW frequency) can be sustained over an extended duration.

RESULTS AND DISCUSSION

Testing the effect of ozone pre-treatment

In order to understand the effect of ozone on the membrane, the pilot was operated without ozone but with PACl coagulation (6 mg/L as Al^{+3}) at 70 and 100 $L/m^2/h$, 30 min filtration time and 9:4:1 backwash sequence. These tests resulted in a rapid rise in TMP for both flux scenarios as illustrated in Figure 2 which shows the 100 $L/m^2/hr$ run over a four-day period. Note that the BW and EBW were only marginally effective at recovering permeability.

In contrast, operation with ozone and coagulation pre-treatment at 100 $L/m^2/h$ seemed very promising, although the operational conditions were difficult to control due to a highly variable feed wastewater quality from the upstream Beenyup WWTP. A decision was made to forgo the coagulant-only trials and undertake all testing with pre-ozone treatment at a setpoint of 0.9 mg/L of ozone residual at the membrane.

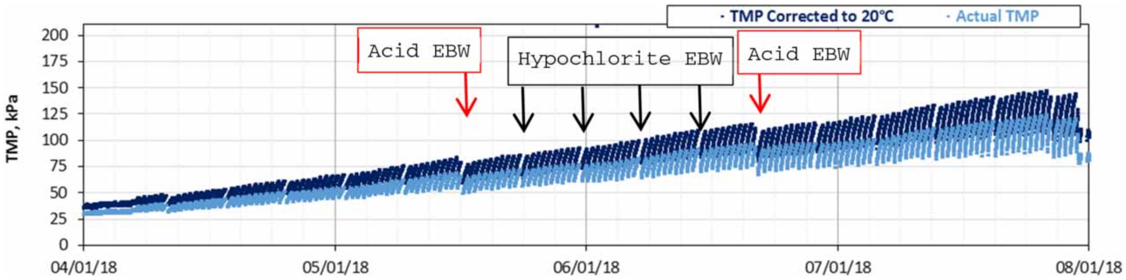

Figure 2 | TMP profile of test run at 100 L/m^2/hr without ozone, 30 min filtration, PACl 6 mg/L Al^{+3}.

Figure 3 shows the run at a flux of 100 L/m^2/h with a 30 minute filtration time. Similar to the run without ozone, the backwash sequence was 9:4:1 and coagulant dose was between 6–8 mg/L (as Al^{3+}). Despite the varying ozone concentrations caused by varying feed wastewater quality an average ozone concentration of 0.8 mg/L was achieved. This regime provided sustainable membrane performance with TMP stable between 25–35 kPa and only a marginal 2–3 kPa increase during the 30 min filtration cycle. The slight increase in TMP towards the end of the run was caused by an interruption in ozone dosing.

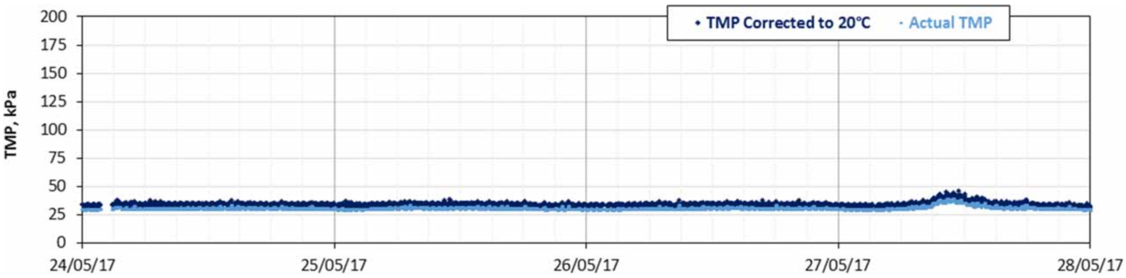

Figure 3 | TMP profile of test run at 100 L/m^2/hr with ozone, 30 min filtration, PACl 6–8 mg/L Al^{+3}.

Establishing critical flux

A series of runs were undertaken to establish critical flux and baseline pilot plant settings. This period ran from August 2017 until December 2017 where a number of design and performance optimisations of the pilot plant were undertaken. Additionally, throughout this period the Beenyup WWTP was suffering variable performance. At times very high turbidity and ozone demand were seen in the treated wastewater feed. Typically, turbidity of the secondary treated wastewater was in the range of 10–25 NTU but there were times when it was exceeding 50 NTU.

Despite the above challenges flux and filtration volume optimisation was achieved to some degree. Increasing TMP or plant shutdown on high TMP was the typical end point of each test. Initially a high flux was set but slowly this was reduced with filtration volume and coagulation dose also adjusted, as per Table 1. During this period the backwash sequence was maintained at 9:4:1.

There were glimpses of good performance at the higher fluxes but often deteriorating feed water quality and/or loss of ozone residual resulted in TMP deterioration. Figure 4 shows the TMP and ozone concentration profile of the test run at 250 L/m^2/hr. It is evident from the figure that a strong inverse correlation exists between ozone residual concentration and TMP, with TMP rapidly increasing to above 100 kPa when ozone concentrations dropped below 0.5 mg/L. Stable operation at 70–80 kPa during filtration cycles was achieved when ozone concentrations were at the 0.9 mg/L (± 2 mg/L) setpoint.

The test runs at 200 L/m^2/hr were short due to the deteriorating feed water quality from the WWTP, which caused high TMP shutdowns, therefore the results are not presented here.

Table 1 | Summary of flux, filtration and coagulation dose test series

Flux (l/m^2/h)	Filtration time (min)	Coagulation dose (mg/L)
250	20	8
200	30	6
150	20	6
150	30	6

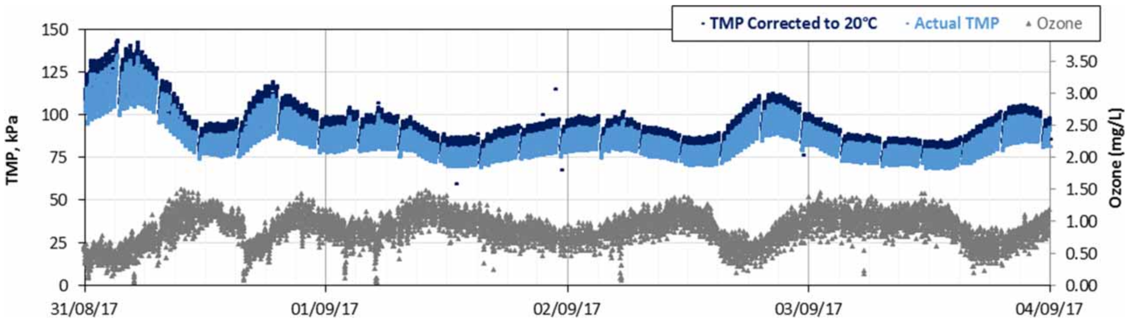

Figure 4 | TMP and ozone profile of test run at 250 L/m^2/hr with ozone, 20 min filtration, 9:4:1 BW sequence, PACl 6–8 mg/L Al^{+3}.

The final flux of 150 L/m^2/hr was seen as a good conservative baseline which gave reliable performance and a sustainable TMP trend without the need for CIP. It should be noted that the good performance achieved at a flux of 150 L/m^2/hr during December 2017 also coincided with significant improvement in the WWTP and much improved feed water quality (<5 NTU). The stable operation at 150 L/m^2/hr, 30 min filtration, PACl dosing of 6 mg/L as Al^{+3}, 9:4:1 backwash sequence and ozone setpoint at 0.9 mg/L can be seen in Figure 5. Ozone concentrations varied during the period, with lower concentrations occurring in the evenings and nights, coinciding with peak flows and slightly poorer effluent quality from the WWTP. The varying ozone is reflected on the TMP profile, which ranged from 27 to 35 kPa. Feed turbidity during the period was <4NTU and pH ranged between 6.7 and 6.8. In all run scenarios, filtrate turbidity was <0.1NTU (~0.05NTU).

It was also suspected that the ozone generator was losing efficiency during this period as its output was mostly at 100% (which should have given 100 g/hr ozone production), despite the improved feed quality at the WWTP. This was later confirmed during a service, which identified a faulty oxygen generator supplying the ozone generator unit.

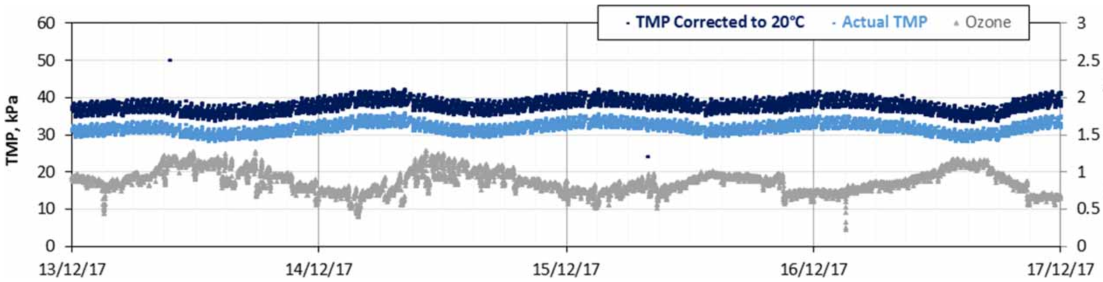

Figure 5 | TMP and ozone profile of test run at 150 L/m^2/hr with ozone, 30 min filtration, 9:4:1 BW sequence, PACl = 6 mg/L Al^{+3}.

Effect of feed pH on ozone concentrations and plant performance

In order to understand the effect of varying pH on ozone concentrations and plant performance, a test run was undertaken with ozone while also maintaining a lower pH with acid dosing (pH set at 6.3). Pilot plant performance was very stable at 150 L/m^2/hr and 30 minute filtration time. Backwash sequence was 9:4:1 and PACl dose at 6 mg/L. The ozone generator was clearly running at a lower output (70–90%) to achieve the target ozone residual (0.9 mg/L). After three days the pH was set at 6.8 and while membrane performance was maintained, the ozone output increased to 100%, suggesting that the lower pH has a positive impact on ozone efficacy (Figure 6).

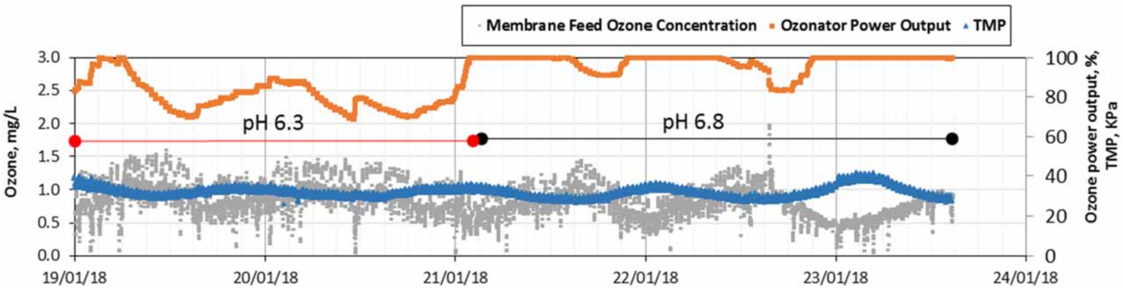

Figure 6 | Ozone concentration, ozone generator output and TMP profile of run at 150 L/m^2/hr, PACl = 6 mg/L Al^{+3}, 9:4:1 BW sequence.

Conversely, an additional short run was undertaken with feed pH set at 7.0 and 7.5 with caustic dosing. This experiment demonstrated that the higher pH caused ozone concentrations to drop to 0 mg/L despite the ozone generator output being at 100%. It is understood that hydroxide ions act as ozone scavengers, reacting with ozone to form hydroxyl radicals (Roth & Sullivan 1983), such that alkaline solutions will rapidly accelerate the decomposition of ozone. The lack of ozone on the membrane caused TMP to rise rapidly and the experiment was terminated (data not shown).

Effect of varying PACl doses

A test run with varying PACl concentrations was undertaken to determine if PACl dosing could be optimised at 150 L/m^2/hr, 30 min filtration, 9:4:1 backwash sequence, pH 6.3–6.8 and ozone concentration (0.9 mg/L). Concentrations of Al^{+3} in the feed were incrementally reduced from 6 mg/L to 2 mg/L and upon signs of steadily increasing TMP at 2 mg/L, PACl dosing was increased to 4 mg/L Al^{+3} to prevent shutdown (Figure 7). Once the optimal coagulant dose was restored, the TMP auto-recovered without any additional cleaning steps or CIP. During the experiment ozone concentrations varied between 0.5 and 1.2 mg/L, with the average being 0.6 mg/L. This experiment confirmed the

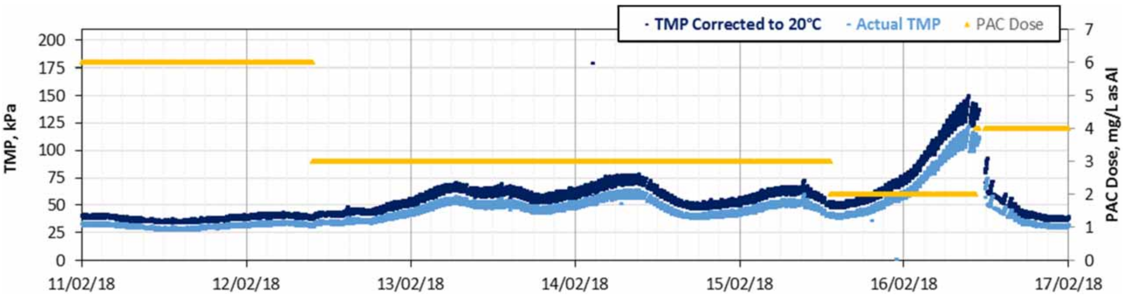

Figure 7 | TMP and PACl dose profile of test run at 150 L/m^2/hr with ozone, 30 min filtration and 9:4:1 BW sequence. Average ozone concentration was 0.6 mg/L for the period.

optimal PACl dosing between 4–6 mg/L Al^{+3}, with potential operation at 4 mg/L, provided ozone concentrations are maintained above 0.6 mg/L.

Increasing doses of PACl up to 10 mg/L were also tested (data not shown) and presented no operational advantage over the 4–6 mg/L operation range in terms of maintaining a low TMP or filtrate turbidity.

Effect of reduced EBW frequencies

After operating the plant at 150 L/m^2/hr with ozone and PACl pretreatment, it was observed that the EBW sequences appeared to have little impact on permeability and maintenance of TMP. A decision was then made to trial operation without EBWs. The TMP and ozone profile for the run without hypochlorite and acid EBWs can be seen in Figure 8 below, which shows stable operation, with the TMP ranging from 30 to 40 kPa and primarily dependent on ozone dosing.

It can be seen that with ozone pretreatment, operation without hypochlorite EBW is sustainable, however, based on PWNT's experience, it is important to maintain the acid EBW in order to prevent calcium, iron and manganese scaling, which can be difficult to remove in the long-term.

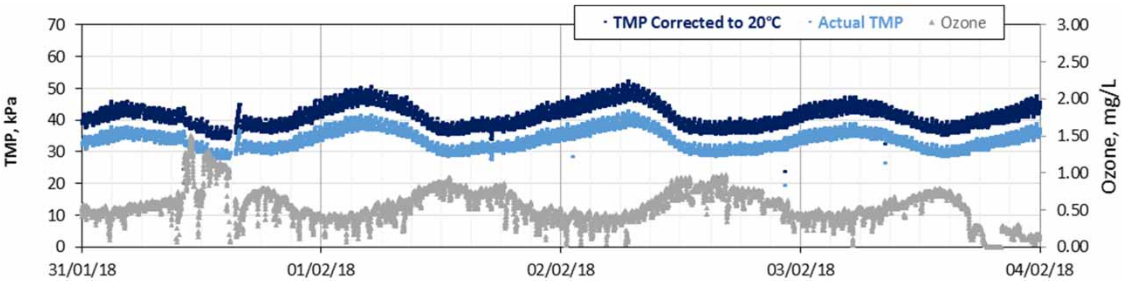

Figure 8 | TMP and ozone profile of test run at 150 L/m^2/hr with ozone, 30 min filtration, normal backwashes only and PACl 6 mg/L Al^{+3}.

CONCLUSIONS

The results thus far have been promising, with sustainable operation at 150 L/m^2/hr flux and possibly higher. Flux rates up to 250 L/m^2/hr were tested but were not sustainable due to bottlenecks elsewhere in the pilot plant, primarily in the capacity of the ozone generator. These flux rates are three to five times higher than comparable achievable flux rates with polymeric UF membranes.

Ozone pre-treatment is the main factor impacting membrane performance. Maintaining an ozone concentration of 0.9 mg/L at the membrane provides sustainable long-term operation at high flux rates. Operation without ozone proved impractical due to rapid fouling of the ceramic membrane surface. This however demonstrated one of the main advantages of ceramic membranes – the ability to use aggressive chemical cleaning regimes (including ozone) to recover the membrane to an as-new state. Recovery from the fouling that resulted when ozone was not dosed was easily achieved without membrane damage through hypochlorite and/or ozone cleaning.

In agreement with the literature (Roth & Sullivan 1983; Hamid 2017) ozone decomposition was fast in slightly alkaline conditions and slower in slightly acidic conditions, favouring operation in a slightly acidic environment (~pH 6.3).

Coagulant pre-treatment using PACl dose ranging from 4 to 6 mg/L as Al^{+3} appeared suitable to sustain long-term operation, with lower doses causing TMP to increase rapidly and higher doses not offering any operational advantage.

One challenge has been the highly variable quality of the Beenyup WWTP secondary effluent. At times, usually over the evening hours, the ozone demand increases to a level that the ozone generator can not maintain a sufficient residual at the membrane surface, thus causing a TMP increase. Some short-term trials at high flux (i.e., 250 L/m^2/hr) have been performed, but long-term operation was generally set at 150 L/m^2/hr to allow reliable 24-hours per day operation.

Now that the Beenyup WWTP performance has improved, giving a more consistent feed wastewater quality, testing at higher fluxes will resume. Performance and cost (capital and operating) comparisons with the installed polymeric UF membranes in the Beenyup Advanced Water Recycling Plant will be undertaken. An early partial assessment of operating cost has indicated that chemical costs for the ceramic MF process are approximately 20% higher than for polymeric membranes. This assessment is based on local (Perth, Australia) chemical supply or production costs and compared:

- PACl, ozone & CIP chemicals for the ceramic membrane, with
- Ammonia, hypochlorite (for mono-chloramine pre-formation) and CIP chemicals for the polymeric membrane.

Future research to more closely monitor filtrate water quality performance will also be undertaken, notably pathogen removal capability.

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