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Production and characterisation of UF membranes by chemical conversion of used RO membranes

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Abstract

Due to the increased use of reverse osmosis (RO) membranes in the water and wastewater industry, large numbers of used modules are expected to be produced in the coming years, and alternative options need to be considered to limit their direct disposal in landfill. One possible solution involves converting and reusing RO elements for ultrafiltration (UF) applications. This study aims to systematically investigate the treatment of used RO elements with 300,000 ppm h sodium hypochlorite (NaOCl) to remove the active polyamide layer thus exposing the microporous polysulfone (PSf) UF support layer. An optimised conversion method is proposed by determining the initial membrane condition and corresponding performance in terms of rejection of proteins and humic compounds, pathogen removal and fouling rate. A number of different membrane types and conditions were studied and their permeability performance varied from 9.3 to 116.3 L m^{-2} h^{-1} bar^{-1} for pre-wetted samples. It was shown that flux recovery of dedicated RO membranes was unsuccessful and that storage conditions and dryness affected the conversion process. The converted membranes demonstrated a 2.4 log removal of virus sized particles, and were comparable to 10 kDa UF in terms of protein and humic substance rejection and fouling propensity. A number of applications and the limitations of this novel concept are also discussed, including preliminary results for a gravity fed drinking water treatment system for decentralised applications.

1. Introduction

1.1. Membrane Lifecycle

In recent decades, the installed capacity of reverse osmosis (RO) water treatment plants has increased considerably worldwide [1,2]. In Australia alone, the capacity has risen from less than 100 ML/day in 1990 to nearly 3000 ML/day in 2012 [3]. Plant expansion is largely attributable to population growth, while decreased process energy costs and improved membrane performance remain critical contributing factors [4–6].

Thin-film-composite RO membranes using aromatic polyamide (PA) are the primary membranes utilised in modern applications for brackish water (BW) and seawater (SW) desalination, as well as domestic and industrial water recycling. Typically, RO membranes consists of a dense PA active layer, a microporous polysulfone (PSf) supporting layer, and a considerably thicker non-woven polyester base [7]. The membranes are generally manufactured by interfacial polymerisation which physically anchors the active and support layers together through interlocking of the pore structures [8]. Current industry consensus suggests that the average lifespan of an RO membrane is between five and ten years, although this is highly dependent upon feed water quality and operating conditions [9,10]. Typical RO processes use approximately one hundred 8” membrane elements per 1,000 m^3/d of product water capacity for a single pass seawater system, requiring tens of thousands of elements to be installed in large plants. Optimising membrane lifespan is therefore critical for plant sustainability and has been the focus of recent investigations [11,12].

In the context of this study, used membranes are defined as modules which have been removed from their primary application due to a decline in membrane performance. Several factors contribute to the decline of membranes performance over its lifetime, and can be manifested by a decrease in permeation, reduction in salt rejection or increase in required operating pressure. These may be as a result of membrane fouling, which over time can be

irreversible and permanently affect membrane performance. The main contributors to fouling include a variety of contaminants such as suspended particulate matter (inorganic or organic), dissolved organic matter, dissolved solids, and biological organisms [13–15]. Oxidative damage can also permanently impair RO membranes, resulting from incidental exposure to chlorine compounds used for water disinfection and fouling removal at various stages of the water treatment process [16,17]. Once in contact with chlorinated oxidants, the active PA layer is degraded through a number of suggested reaction pathways including N-chlorination of amine groups and aromatic ring chlorination, which can be summarised as the weakening of PA intermolecular hydrogen bond interactions with the incorporation of chlorine [18,19]. In addition, limited evidence has also been presented that the supporting layers of the membrane were unaffected by moderate chlorine exposure [20].Another significant factor affecting membrane performance is the method used for storage and transportation. Manufacturers generally recommend soaking the element in 1% food-grade sodium metabisulphite solution and storage in a sealed bag to maintain membrane hydration and to preserve performance [21,22]. Failure to adequately preserve and store membranes can lead to premature drying of the element and permeability loss resulting from increased interchain hydrogen-bonding replacing the water-polymer bonds which facilitate permeation [23].

In addition to optimising the lifespan of RO membranes, consideration of the reuse, recycling and disposal of membranes could elicit further improvements in the sustainability and cost-effectiveness of desalination and water recycling plants. In Australia, RO membranes will ultimately be disposed in landfill, and considering the expanding industry, the mass of disposed membranes is expected to rise to 800 tonnes/year by 2015 [3,24]. In order to minimize the environmental impact of membrane disposal, alternative uses for end-of-life membranes are therefore required.

1.2. Options for Membrane Reuse and Recycling

Several options are currently considered for RO membrane reuse. Two applications previously addressed include recycling material components and reducing the waste impact of disposed membranes [25]. A methodology currently under investigation also considers the repurposing of RO membranes for secondary applications [24].

In a recent study, used RO element performance was assessed and compared to new membranes. Although all studied membranes showed more than 96% NaCl rejection, they were no longer in accordance with the original performance criteria of >99.5% rejection. However, the authors proposed that the residual high level of salt-rejection would facilitate direct membrane reuse in alternate applications such as brackish water treatment [26]. Additionally, the reuse of old RO membranes was examined by assessing their functionality and level of ageing. Autopsy techniques were used to assess hydraulic permeability, salt rejection, morphological and topographical variations, as well as the presence of chemical or biological elements. Overall, it was concluded that the used RO elements featured similar specifications to nanofiltration membranes [27].

The aforementioned studies examined the direct reuse of RO membranes without additional membrane modification. However, radical chemical treatment on used RO membranes could facilitate conversion for additional applications. The effects of oxidative degradation and long-term chlorine exposure have been well documented [18,19], and the literature suggests that removing the active layer of a retired RO membrane via oxidative degradation has the potential to result in a separation device that has a similar physical structure to standard polyethersulfone (PES) UF membranes [28–30]. This technique of oxidative chemical treatment to remove the PA active layer of the RO membrane resulting in an UF membrane is referred to as membrane conversion.

This method of RO conversion was first explored in 2002 [28], when chemical treatment by potassium permanganate ($KMnO_4$), NaOCl and sodium hydroxide (NaOH) was used to

attempt conversion of retired RO modules, for reuse in wastewater pre-treatment [31]. While only low doses of the chemicals were used, it was concluded that $KMnO_4$ treatment facilitated the most extensive removal of the active layer. Importantly, the study reported that the treated membranes displayed adequate performance in subsequent applications within municipal wastewater treatment. The membranes were capable of a 93.9% average reduction in turbidity [27], however, fouling was identified as a significant problem in the application of converted RO membranes although this was not systematically studied.

A recent study by Ambrosi et al, again assessed the viability of conversion using $KMnO_4$ treatment, and displayed that it is possible to obtain stable performance resulting in high permeate flux at the expense of lower salt rejection [32]. A cleaning step with citric acid was investigated to address a decrease in permeability due to the formation of a manganese oxide layer, formed from the oxidative treatment. This study has shown that even the most effective $KMnO_4$ treatment resulted in only a 2 fold increase in permeability with salt rejection reduced to 85%. Moreover, it has not been clearly demonstrated that this techniques completely removes the active layer of the membrane and therefore presents limitations for RO conversion into UF.

Considering the limitations in the use of KMnO4 in active layer removal, the current authors sought to examine the most effective removal treatment [24]. The solutions tested for their removal performances include NaOH, $KMnO_4$ and NaOCl, with exposure intensities ranging between 28,000 and 500,000 ppm h. The resulting membranes were tested for pure water permeability and salt rejection and it was concluded that the active layer was completely removed when further treatment did not result in an increase in permeability. The results showed that NaOCl was the most successful degrading agent with exposures of 100,000 and 300,000 ppm h, using concentrations of 6.25% (w/v) for 2 h and 0.625% (w/v) for 48 h respectively, resulting in stable flux and average salt rejections below 4%. The removal of the PA active layer was confirmed with surface morphology analysis using scanning electron microscopy (SEM) [25]. Both $KMnO_4$ and NaOH treatment resulted in a significant effect on

salt rejection, indicating discernible damage to the membrane surface. However, flux increase was an order of magnitude lower than NaOCl treatment, suggesting that complete removal of the active layer was not achieved. As a result, an exposure of 300,000 ppm h of NaOCl was recommended as the standard protocol for the continuing investigation of RO membrane conversion. A similar methodology has been used in a recent study to convert seawater RO (SWRO) membranes with NaOCl into brackish water RO (BWRO) and to briefly consider the formation of UF membranes through prolonged exposure [33]. Exposure intensities from 7,000 to 300,000 ppm h were tested, and the results were consistent with the effects of prolonged exposure discussed in Lawler et al [24]. Furthermore, these two recent studies found comparable permeability and rejection characteristics of the converted membranes. Although preliminarily addressed in the previous work by the current authors [25], the main limitation of these studies was the limited characterisation of membranes properties and susceptibility to fouling. Moreover, discussion of the effect of used membrane condition on subsequent converted performance has not yet be presented and converted RO membranes are still to be benchmarked against commercially available UF membranes. Finally, Raval et al's examination of NaOCl treatment only utilised membranes manufactured in house for the prolonged exposure tests, with limited discussion of the potential applications of the the converted membranes.

1.3. Optimisation of conversion protocol

The aim of the current study is to build on previously published work and systematically investigate opportunities for RO membrane reuse by: (a) determining the optimum protocol for converting RO membranes, including the effect of storage conditions as identified in preliminary study; (b) examining the effect of active layer removal on flux, rejection and surface morphology on a range of virgin and industrially used membranes; (c) benchmarking the efficacy and fouling of converted RO membranes against UF membranes and (d) discussing and investigating potential applications and limitations of the converted RO membranes.

2. Materials and Methods

2.1. Membranes

The characteristics of the membranes used in this study, including UF, SWRO, and BWRO are summarised in Table 1. All RO membranes tested were PA thin-film composite construction with a PSf support layer, and have a manufacturer stated chlorine tolerance rating of less than 1,000 ppm h or a continuous free chlorine exposure of less than 0.1 mg/L.

Table 1: Condition and key properties of studied membranes.

Label	Membrane	Manufacturer NaCl Rejection	Type	Condition	Initial permeability (L m^{-2} h^{-1} bar^{-1})
DOW	DOW BW30FR	99.5*	BWRO	Virgin/dry	3.5
Koch1	Koch 8822HR	99.5*	BWRO	Used/wet	2.8
CSM	CSM RE8040-FE	99.5*	BWRO	Used/moist	3.31
Hydra	Hydranautics CPA5-LD	99.7#	BWRO	Used/moist	0.45
Toray	Toray TML820	99.7^	SWRO	Used/moist	0.32
Koch2	Koch TFC-SW	99.75^	SWRO	Virgin/dry	0.8
UF	10 kDa flat sheet PAL Omega PES UF	-	UF	Virgin	120

* 2000 ppm at 15.5 bar, 15% recovery
# 1500 ppm at 15.5 bar, 15% recovery
^ 32000 ppm at 55 bar, 8% recovery

2.2. Membrane Wetting and Conversion

For this study, the conversion method was as follows: membrane samples were cut to size from sheets of spiral wound elements and pre-conversion wetting was applied. Wetting and testing was undertaken using a Sterlitech HP4750 high pressure dead end cell with Milli-Q™ water and pressure was applied using a nitrogen cylinder. Following the wetting step, samples were exposed to a NaOCl solution which was protected from UV light to minimise NaOCl deterioration. The samples were exposed to the solution for 2.4 h at room temperature. The NaOCl used was 12.5% w/v technical grade from Ajax Finechem Pty Ltd and the concentration was determined spectrophotometrically at a wavelength of 292.5 nm using a molar extinction coefficient of 360 $M^{-1}cm^{-1}$ [34]. The pH of the solution was

maintained at 12 ± 0.5. Following conversion, samples were thoroughly rinsed and then stored in Milli-Q™ water at 4°C prior to characterisation.

2.3. Membrane Characterisation by FTIR

Membrane samples were characterized by Fourier transform infrared (FTIR) spectroscopy using a Shimadzu IRAffinity-1 FTIR spectrophotometer. The membranes were analysed by attenuated total reflectance (ATR) using a Pike Technologies VeeMAX™ II variable angle specular reflectance accessory using a 45 degree ZnSe ATR crystal. The spectra were recorded at a resolution of 4.0 cm^{-1} in the range 4000-600 cm^{-1} with an average of 56 scans per membrane.

2.4. Rejection Characterisation

Salt rejection characterisation was conducted using 2000 ppm of NaCl (Sigma Aldrich, Australia) at 15 bar for RO and 1 bar for converted RO in the aforementioned dead end cell. For advanced rejection characterisation, a solution of 10 mg/L humic acid (HA) and 10 mg/L bovine serum albumin (BSA) (Sigma Aldrich, Australia) was passed through membrane samples and analysed using liquid chromatography-organic carbon detection (LC-OCD), system model 8, based on the Gräntzel thin film reactor developed by DOC Labor, Germany [35].

2.5. Silver Nanoparticle Challenge Testing

Citrate stabilised silver nanoparticles were prepared by dissolving 9 mg of silver nitrate in 50 mL of water and bringing to boil. To the boiling solution, 1 mL of 1% sodium citrate solution was added dropwise under vigorous stirring. After complete addition, the mixture was further boiled for 1 h and allowed to cool at room temperature. The mixture was centrifuged at 25000 rpm for 30 min to separate the nanoparticles from the free silver ions. The nanoparticles were then redispersed in water by sonication and stored for testing. All the

reagents used to prepare the nanoparticles were of analytical grade and Milli-Q™ water was used throughout experiments. The particles were filtered through the membrane samples using the setup described in Section 2.6, feed and permeate samples were collected after 15 and 30 min of operation and analysed for Ag content by Perkin Elmer optima 7300 inductively coupled plasma (ICP) optical emission spectrometer.

2.6. Fouling Characterisation

Fouling and cleaning experiments were performed using a laboratory-scale cross flow unit, which allows for long-term automated cycles. The tests used 0.5% w/v NaOCl cleaning solution and mixture of BSA, humic acid (HA), alginic acid (AA), colloidal silica and calcium carbonate (sourced from Sigma Aldrich, Australia) as synthetic feed. Before filtration, the flat sheet module and all membranes were rinsed with Milli-Q™ water at 30 L m^{-2} h^{-1} for 30 min prior to the synthetic feed testing. Cole-Parmer Masterflex peristaltic pumps provided up to 2 bar of transmembrane pressure (TMP), recorded by pressure transducers, located across a custom built plate and frame membrane cell featuring an active surface area of 0.00275 m^2. In addition, contact angle measurements were made using the sessile drop method [36].

3. Results and Discussion

3.1. Effect of storage conditions on hydraulic performance

The membranes used in this study, were in a variety of conditions (i.e. wet, moist or dry) resulting from their different usage and storage history. In order to assess the potential impact of membrane drying during storage, two membranes (DOW and Koch1) were tested for permeability before and after artificial desiccation. In the case of the virgin dry DOW membrane, initial wetting was done in order to simulate use and assess compaction. Drying was achieved in a desiccator for 24 h and Milli-Q™ water under 15 bar pressure was used for the wetting steps. The permeability change (in L m^{-2} h^{-1} bar^{-1}) over time is presented in Figure 1.

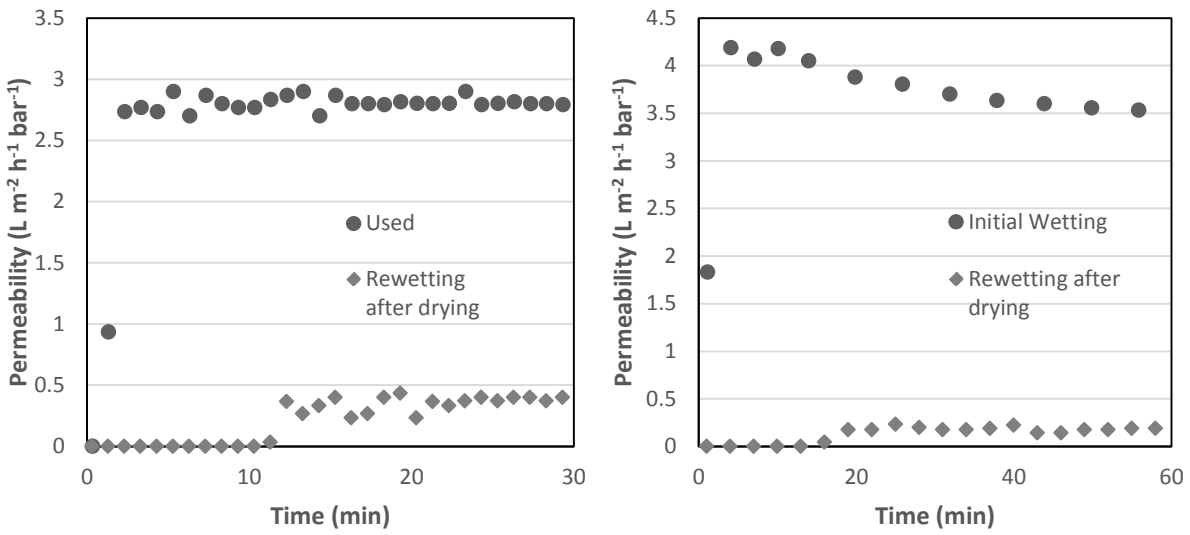

Figure 1: Average permeability trend of membranes under varying storage conditions (15 bar, Milli-Q^{tm}). Left: Koch1 Right: DOW.

The Koch1 samples, which had been stored wet, quickly reached and maintained a stable flux of 2.8 ± 0.3 L m^{-2} h^{-1} bar^{-1}. On the other hand, the dried samples took over 10 min to produce any permeate and the resulting permeability was significantly lower at 0.39 ± 0.2 L m^{-2} h^{-1} bar^{-1}. The case with DOW is slightly different, as the membrane had not been wetted before. As a result, the initial wetting stage starts off at a slightly higher permeability but

gradually declines and stabilises as compaction of the dense PA layer occurs. Rewetting attempts were even less successful than with the Koch samples, as it took up to 20 min for any permeate to be produced and resulted in a permeability of only 0.2 ± 0.1 L m^{-2} h^{-1} bar^{-1}. The mechanism for this phenomenon is likely to be the reduction of water-polymer interactions or by collapsing of pores via capillary forces, driven by the evaporation of water [23]. Rehydration becomes difficult once the pores collapse, resulting in significantly lower hydraulic performance, while theoretically retaining rejection properties. The NaCl rejection of the dried samples was tested and no statistical difference was observed. DOW that had not been subjected to the initial wetting stage (i.e. dry as purchased) all was also desiccated and then wetted, however no noticeable difference in permeability was observed compared to the initial wetting stage of samples represented in Figure 1. This supports the idea that it is the evaporation of water from the moist pores which closes them, as the DOW membrane was purchased and delivered dry, without a preserving agent. These results show that the permeability loss of wet membranes subjected to desiccation, is irrecoverable using the described method. Therefore, the importance of proper membrane storage in order to maintin hydraulic performance is highlighted as the dry membranes resulted in a lower average permeability than the membranes that were stored wet (or compared to new samples).

A typical method recommended by manufacturers for effective re-wetting requires membrane pressurisation at 10 bar while the permeate valve is closed [37]. This method was tested at length, however no detectable additional performance was observed. Other recommended methods for re-wetting dried elements include soaking in 50/50% ethanol/water solution for 15 min or in 1% HCl or 4% HNO_3 for 1-100 h [37]. Rewetting a RO membrane via soaking in ethanol has been previously explored and was shown to partially restore the initial flux [23]. Although these methods do not require a filtration system, they increase the consumption and subsequent disposal of additional chemicals.

3.2. Impact of Pre-wetting on Conversion Efficiency

To assess the variation in performance of converted membranes, the process was applied to a range of virgin and used BWRO and SWRO membranes. The effect of membrane pre-wetting was assessed by applying the process to samples left as stored and with additional wetting. In addition, some membranes were converted after desiccation, with and without attempted rewetting, to simulate the worst case scenario for stored membranes. Six different types of membranes (2 virgin and 4 used) were converted in both original and wetted states. The wetting was conducted at 15 bar for 30 min and the conversion was based on a NaOCl exposure of 300,000 ppm h. After conversion, the samples were tested for permeability at a range of pressures (0-4 bar).

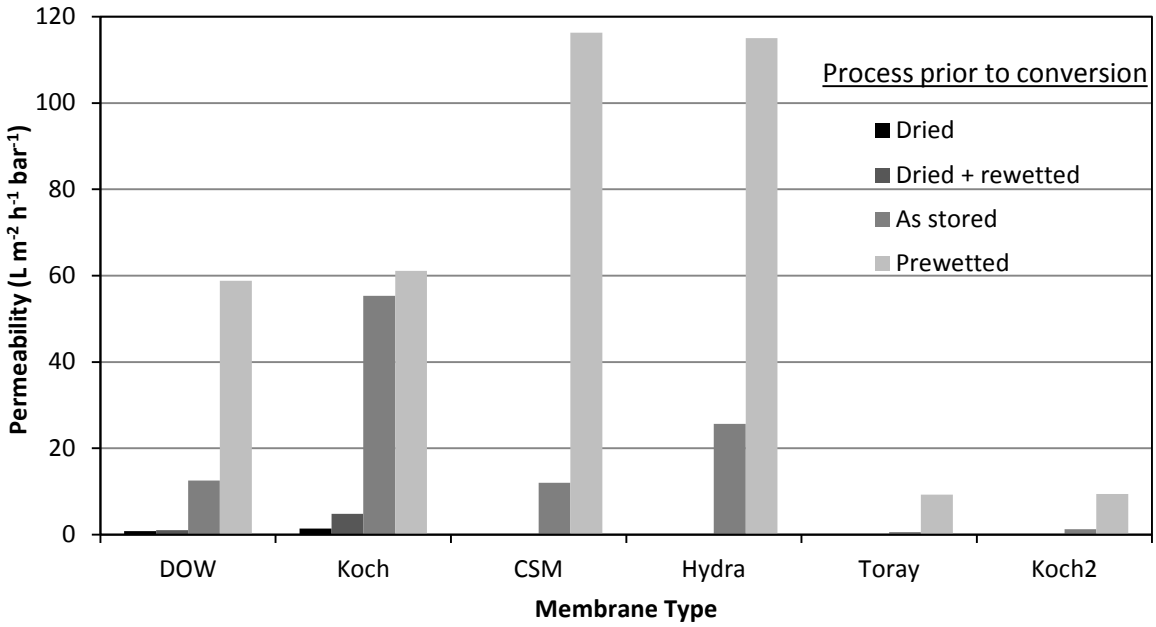

Figure 2: Effect of wetting (at 15 bar) on conversion efficiency (Permeability tested at 0-4 bar).

As shown in Figure 3, the pre-wetted membranes obtained up to a 14 fold increase in permeability when compared to the un-wetted membranes; however, there was great variation in performance from the different membrane types. The virgin DOW showed a 370% increase in permeability when wetting was applied, while Koch1 which was stored wet achieved only 10% increase with additional wetting. DOW and Koch1 showed extremely

poor converted performance when completely desiccated, even with attempted rewetting; however, there was still a measurable increase in permeability over their unconverted RO state. Due to the significantly lower converted performance of the desiccated samples when compared to wet samples, these tests were not conducted with the other membranes. However, the results obtained clearly indicate that membrane drying is detrimental to the success of the conversion process. The salt rejection for all converted membranes was tested, showing less than one percent removal. This suggests that the PA layer was still significantly compromised on these low performance membranes. One proposed mechanism for the performance difference between the wet and dry samples is that increased inter-chain hydrogen bonding which occurs during drying, subsequently affects the process of ring chlorination. In addition, it is possible that the voids collapsing via capillary forces during the drying process inhibit the penetration of the oxidising solution, thus reducing its effectiveness [23].

The two SWRO membranes, Toray and Koch2 showed an extremely low converted performance, with and without pre-wetting. Toray was stored moist and Koch2 was a virgin dry sample that had not been previously wetted. While converted performance was low compared to the BWRO samples, the membranes showed a minimum of 2 fold increase in permeability after conversion and pre-wetted samples reaching over 9 L m^{-2} h^{-1} bar^{-1}. Conversely, two of the BWRO membranes (CSM and Hydra), which were extremely fouled/damaged and had previously been used for coal seam gas water treatment applications, showed a significant increase in permeability (8.6 and 3.5 fold respectively) when pre-wetting was applied. Comparably, a previous study obtained a converted flux of 124 L m^{-2} h^{-1} bar^{-1} when applying a similar conversion protocol (300,000 ppm h of NaOCl exposure) to an in house manufactured PA/PSf TFC SWRO membrane, following a wetting phase [33].

The different performances between the converted SWRO, BWRO and damaged membranes, indicate that converted performance is affected, not only by storage conditions,

but also by the membrane condition and construction. The difference in membrane type, manufacturer, and the degree and nature of the fouling/damage can potentially affect the resulting performance. Supporting this concept, it has been shown that different PSf construction methods and additives can affect the hydraulic performance of the support layer [30]. Additionally, it is possible that further degradation of un-wetted samples would result in hydraulic performances comparable to the wetted samples, however this was not explored in the current study. This variability in performance is expected to be an issue when using this conversion method for specific reuse applications as membrane properties will need to be carefully evaluated on a case-by-case basis with testing required for each individual module source.

Another possible application of this treatment method is to use controlled exposure with NaOCl to partially remove the active layer, trading increased permeability for decreased salt rejection, resulting in a nanofiltration or high flux BWRO membrane. Based on work shown here and previously published [24,33], it has been concluded that this controlled removal of the active layer is possible but challenging. This is due to the varied response of different membrane types to the conversion process and the rapid removal of the active layer as exposure time increases. Implementation of this technique would require the testing of optimum exposure for each membrane type and is unlikely to lead to consistent flux and rejection performance.

The additional step of membrane wetting prior to conversion, is unfavourable in terms of operation time, energy and required equipment. Therefore, an important consideration is the minimum pressure of wetting required to achieve favourable results. To determine the optimum pressure range, the virgin BOW samples wetted at different pressures were converted using the standard method and tested in order to determine the relationship between wetting pressure and hydraulic performance (Figure 3).

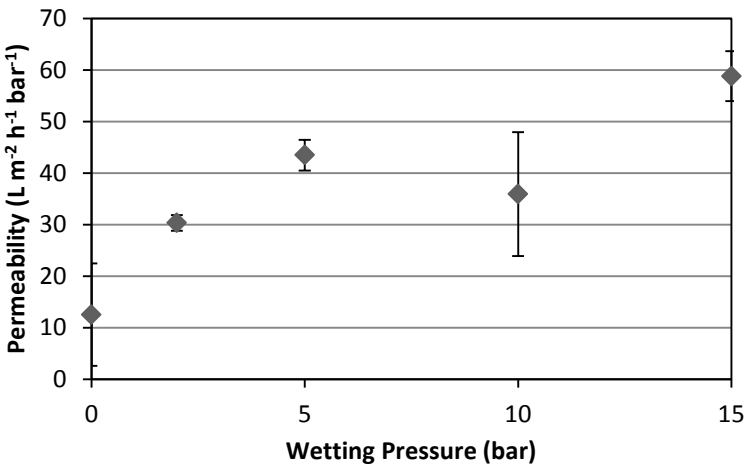

Figure 3: Performance of resulting converted DOW after treatment at various wetting pressures (Resultant permeability tested at 4 bar).

As expected, it was observed that as wetting pressure increased, so did the resulting permeability, with a plateauing trend developing at higher pressures. Wetting at 2 bar results in over twice the permeability of the dry samples, and the hydraulic performance continues to improve up to 5 bar of applied pressure. Large sample variability was observed during the triplicate analysis and the appropriate errors have been displayed. The overall trend indicated performance up to of 59 ± 5 L m^{-2} h^{-1} bar^{-1} for 15 bar of prewetting pressure. The results indicate that increasing the wetting pressure of the used RO membrane improves the hydraulic performance of the converted membranes.

3.3. Active layer removal

During preliminary investigation, visual inspection with SEM was used to confirm the successful removal of the active layer [25]. To further support the evidence of conversion, chemical changes in the PA layer were investigated by FTIR spectroscopy. In Figure 4, a select range of FTIR spectra for virgin and converted pre-wetting samples of DOW membrane are shown.

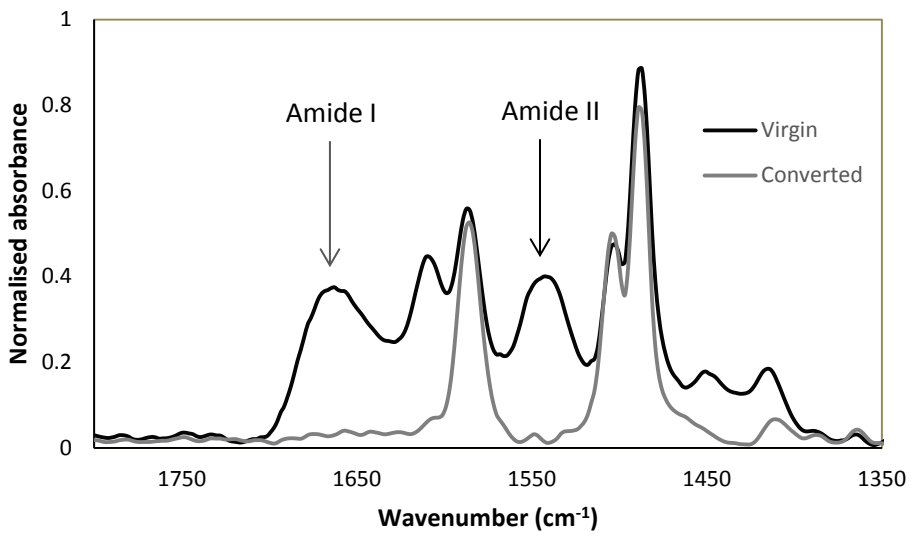

Figure 4: Infrared spectra of DOW membrane, virgin and exposed to 300.000 ppm h of NaOCl.

The spectra from the untreated membrane shows peaks at 1667 and 1542 cm^{-1}, corresponding to amide I and amide II bands respectively, and are associated with predominately C=O stretching and N-H plane bending [20]. The peak at 1610 cm^{-1} is representative of the C=C stretching vibrations from the aromatic amide bonds [20,38]. The converted membrane exhibits suppression and possibly elimination of the characteristic aromatic polyamide peaks which has been previously shown to be an indication of chlorine damage via the mechanism of Orton rearrangement [18]. When comparing these results to previous studies on free chlorine damage to PA membranes, the relative peak suppression is extreme and nearly complete [19,39], a difference which can be explained by the significantly higher oxidant exposures used. This suppression corresponds to breaking of various bonding groups and the subsequent deterioration of the chemical structure. The peak at 1487 cm^{-1}, which corresponds to a characteristic peak of PSf (CH_2 stretch), does not show any significant suppression. The PSf peaks can be seen in the spectra of the membrane due to the relatively deep penetration of the light probe compared to the PA layer thickness. This lack of suppression indicates that the PSf layer has not been negatively affected in this band by the conversion process [19].

Based on this qualitative assessment, the PA active layer has undergone significant changes to its chemical structure. Along with the changes in salt rejection and hydraulic performance presented both here and in previous work and with visual confirmation via SEM analysis [25], it is suggested that the conversion process results in substantial and possibly complete removal of the PA layer from the underlying membrane support layers.

3.4. Rejection Properties

Challenge testing was used to contrast the rejection performance of converted RO to commercially available UF membranes, which were selected due to similar hydraulic performance, and to estimate the molecular weight cut-off (MWCO) of the newly converted membranes. A solution of proteins and humic substances were filtered and analysed by LC-OCD [35] (Figure 5).

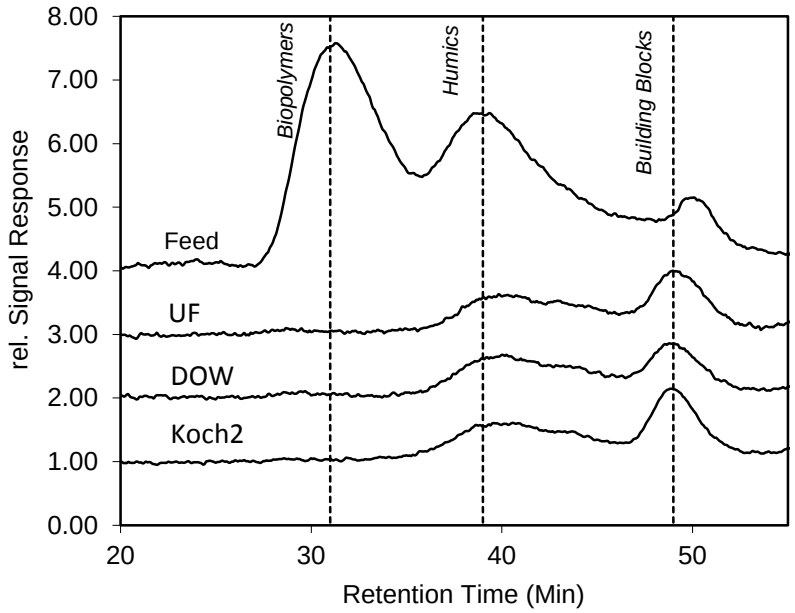

Figure 5: LC-OCD chromatogram for protein and humic feed and permeates from UF (10 kDa) and converted RO (DOW and Koch2).

The prominent biopolymer peak of the feed solution shows a high content of substances with a molecular weight of above 10kDa. The right boundary of the biopolymer peak is defined by

the start of the humics peak, which is also pronounced in the feed solution samples (between 10 and 1 kDa). The final peak displayed is related to the building block materials, low molecular weight acids and neutral components originating from the breakdown of protein compounds (less than 1kDa). For all filtered samples, both the biopolymer and humic peaks were suppressed, indicating their efficient removal and all membranes tested exhibited a biopolymer rejection above 97%. In addition, the rejection of humic substances is similar between the various samples, with 69% of humics retained by the PES UF membrane and the converted RO membranes rejecting between 63 and 67%. As described previously, the DOW membrane demonstrated a permeability more than 5 times higher than that of the Koch2, while still presenting comparable rejection performances. Using this comparative method, the MWCO for the converted RO membranes was estimated to be similar to the tested UF membrane, i.e. around 10 kDa.

3.5. Pathogen Removal

To confirm the converted membrane rejection properties, further investigation into pathogen removal by challenge testing was conducted to enable a more effective suitability assessment for possible water treatment applications. Citrate stabilised silver nanoparticles were used as a virus analogue and were selected based on consistency, ease of manufacture and testing. Particles were filtered in a cross flow configuration, followed by analysis of the permeate using ICP. The membrane removal efficacy was calculated as log removal value (LRV):

$$LRV = -log_{10}\left[\frac{C_{in}}{C_{out}}\right]$$

Where C_{in} and C_{out} are the average particle concentrations in the feed and permeate respectively. The results and calculated LRVs are displayed in Table 2.

Table 2: ICP results from Ag model virus particle removal.

Membrane	Feed concentration mg Ag /L	Permeate concentration mg Ag /L	Rejection (%)	LRV
Converted DOW	9.19	0.035 ± 0.009	99.62	2.42
10kDa UF	8.05	0.024 ± 0.003	99.75	2.57

The 10 kDa UF and the converted DOW membrane displayed rejections above 99.5%, equivalent to LRVs of 2.57 and 2.42 respectively for the tested particles. Previous work conducted by our research group has revealed that the particles closely resemble the physical characteristics of some water-borne viruses. Specifically, the particles were 62 ± 10 nm in size, had a strong negative charge of -25±4 mV and were nearly spherical in shape [40].

These rejection values are slightly low when compared to other direct integrity testing methods including the commonly used MS2 bacteriophage. For example, this indicator has

been shown to demonstrate an LRV of 3-4 for hollow fibre UF membranes of similar MWCO values [40]. However, as operating conditions significantly affect LRVs, evaluating different methods can be difficult and further testing is required to adequately compare the various techniques. Ultimately however, the results indicate that the conversion process has not compromised the integrity of the microporous UF supporting layer of the original RO membrane or its ability to remove virus-sized compounds from the feed water.

3.6. Fouling Propensity

Fouling remains a major cause of membrane productivity loss and often dominates the design and operation of treatment systems. To investigate the fouling potential of the converted membranes, accelerated long term filtration experiments were performed using both converted DOW and commercially available flat sheet UF membranes for comparison. A solution modelling river water with high organic content (TOC of 20 mg/L) was used to accelerate fouling and cross flow cleaning was conducted using sodium hypochlorite. The aim was to determine if the exposed PSf surface of the converted membrane was specifically vulnerable to fouling due to increased roughness or resistance to cleaning.

Figure 6 shows a typical series of fouling and cleaning cycles from a converted RO membrane. The plot illustrates the change in TMP expressed as fouling rate ($\Delta TMP/\Delta t_{cycle}$) for each filtration cycle, as well as the overall TMP rate increase during the entire filtration period ($\Delta TMP/\Delta t_{overall}$). The results demonstrate a consistent fouling gradient for each cycle, as well as an overall increase in TMP. Following each fouling cycle, the cleaning cycle was shown to partially recover the TMP increase caused by fouling build-up.

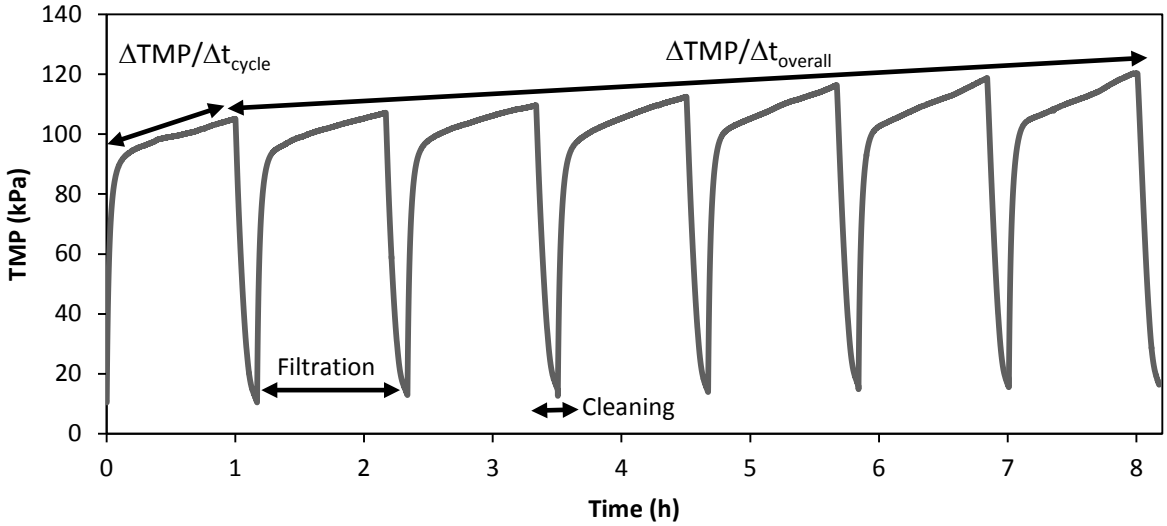

Figure 6: Depiction of fouling effect for 60 min filtration and 10 min cleaning cycles at 30 L m^{-2} h^{-1}.

Figure 7 shows the TMP behaviour over 32 cycles of 70 min each for the two membrane types tested. To assess the effectiveness of the cleaning cycles, cleaning efficiency (CE) was calculated using:

$$CE = \frac{\Delta TMP_{cycle} - \Delta TMP_{Residual}}{\Delta TMP_{cycle}}$$

Where ΔTMP_{cycle} is the TMP increase during the each fouling cycle and $\Delta TMP_{residual}$ is the unrecovered TMP increase after the cleaning cycle. Table 3summarises the TMP and cleaning efficiencies during consecutive cycles.

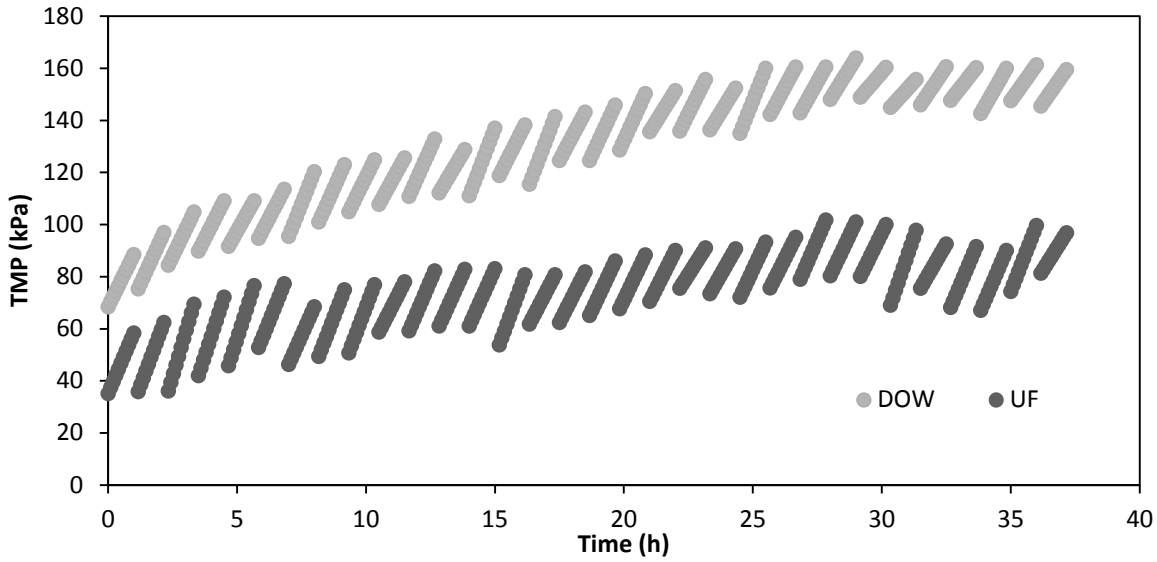

Figure 7: TMP behaviour during cyclical fouling and cleaning.

Table 3: Cleaning efficiency and changes in TMP.

Membrane type	ΔTMP/Δt cycle average (kPa/h)	ΔTMP/Δt overall (kPa/h)	Average cleaning efficiency (%)
Converted DOW	18.6	1.81	86.4
UF	22.6	1.01	91.7

The membrane resistance of the UF and converted RO was initially calculated as 0.30 and 0.58 × 10^{13} m^{-1} respectively. As fouling occurs during each cycle, a TMP increase was observed and this was partially mitigated during each subsequent cleaning cycle as the cleaning protocol removed the reversible fouling build-up. Over the course of the experiments, the overall TMP increase was consistent as a result of irreversible fouling build-up, which was not recovered during the hypochlorite cleaning cycles. However, as the silica and calcium carbonate components of the feed do not respond to the hypochlorite cleaning, further TMP restoration could be realised with an acidic clean.

The overall TMP increase was 1.8 and 1.0 kPa/h for the converted and UF membranes respectively, showing a greater build-up of irreversible fouling on the converted membranes over the same time period. The commercially available UF membrane featured an average TMP increase per cycle of 22.6 kPa/h compared to the converted membrane rate of 18.6

kPa/h, suggesting that the UF membranes fouled at a slightly faster rate during each filtration cycle. Results by Hajibabania et al obtained using a similar protocol, model solution and hollow fibre PVDF membranes, showed a comparable average fouling rate of 31.2 kPa/h [41]. The difference in cleaning efficiency explains how the converted membranes fouled at a slower rate per cycle but faster overall. On average, the cleaning process was 92% effective for the UF membranes, but only 86% effective for the converted membranes, suggesting that while the UF membranes fouled faster, they were cleaned more effectively leading to a lower increase in $\Delta TMP/\Delta t_{overall}$. Due to the extreme nature of the chemical treatment removing the physically interlocked PA layer from the PSf support, it is expected that converted RO would have a higher fouling propensity than commercially manufactured UF, resulting from high surface roughness and other altered surface properties. Average surface roughness of membranes can affect its fouling propensity and can be determined by atomic force microscopy (AFM). While not currently addressed, future work will assess the effect of NaOCl treatment on the roughness of the resulting UF membrane as a prediction tool for fouling. In practice, under the relatively extreme fouling conditions imposed during this study, the converted membrane did show a higher fouling propensity and cleaning resistance, but not to the degree that was initially hypothesised.

Furthermore, contact angle measurements determined that the 10 kDa UF membrane was more hydrophobic at 83 ± 1° than the converted RO membranes at 70 ± 3°. This difference in hydrophobicity, along with the potential difference between the protein affinity of the PES construction of the UF membrane and the PSf construction of the converted RO membrane, could also make a significant difference in fouling performance [42].

An important consideration, not explicitly addressed in these experiments, is the effect of the feed spacers on membrane fouling. Feed spacers can limit the deposition of gel particles and reduce concentration polarization [43,44], while promoting biofouling growth [45]. Further consideration of the effect of the thinner RO feed spacers on UF applications is

required as these may be susceptible to clogging or increased fouling, especially with feed of high suspended solids.

Within the operating conditions of this study, the converted membranes did not suffer from catastrophic fouling rates. However, they are still quite susceptible to resistance increases and when compared to a commercially available UF membrane, did not respond as favourably to a basic cleaning modality. The differences between the performance of converted RO and manufactured UF will be an important consideration when seeking potential applications for the converted membranes.

3.7. Potential Applications

The results of this study show that converted membranes have promising technical performance, making them potentially suitable to replace flat sheet UF membranes for a wide range of applications. These include the emerging applications of RO pre-treatment [46,47], water disinfection [48] and advanced industrial and residential wastewater treatment [49]. Other common UF applications in the food and pharmaceutical industry would be a challenge for converted membranes, as their unsanitary nature will make compliance with the relevant regulatory agencies difficult [50]. However, in the case of advanced wastewater treatment and desalination pre-treatment, converted RO modules are expected to remove all suspended solids, large organic species, and a significant fraction of pathogens present in the feed. The variation of results from converting different membrane types signifies that further validation and integrity testing will be required to assess the performance of each membrane batch.

One application currently under investigation is their use in gravity driven membrane water treatment, for use in rural communities and developing countries. Preliminary tests using a ground water analogue feed solution, a custom designed plate and frame setup with a surface area of 0.12 m^2, and a maximum hydraulic head of 1.4 m showed promising results.

The system operated in a submerged configuration, using gravity driven hydraulic pressure as the driving force.

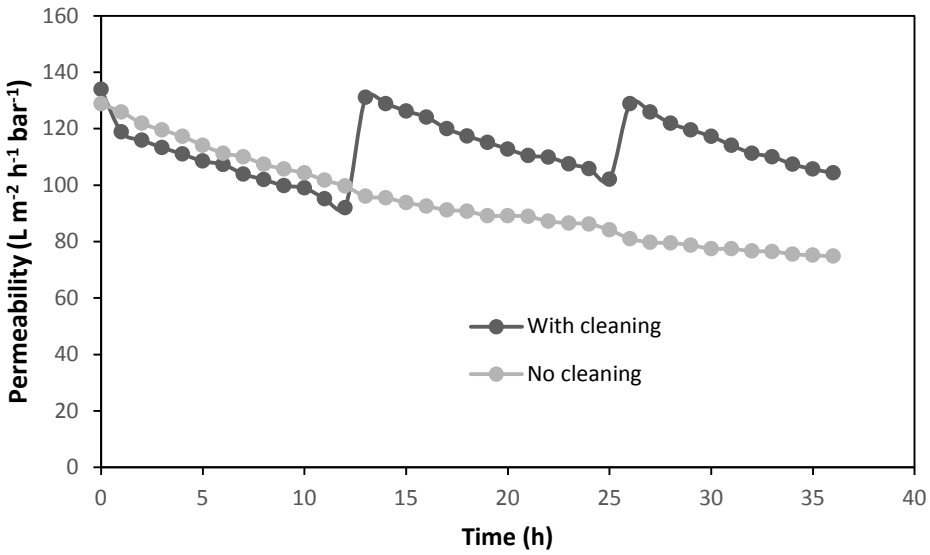

Figure 8: Permeability decline of converted DOW membrane used in gravity driven membrane treatment.

Figure 9 shows the permeability loss experienced by the system over a period of 36 h, as well as the effect of simple cleaning methods. For each cleaning cycle, the membranes were removed and wiped with a sponge until visible build-up was removed, resulting in a substantial recovery of permeability. This cleaning method, while effective in the current configuration, would not be possible if the membranes were used as a spiral wound module. This simple cleaning method, which is manageable by an untrained operator, allows for the long term operation of the system and the effective restoration of flux.

In a 24 h period, the system produced 19.4 L of water which is considered enough to supply water to a family of four in developing communities [51]. In addition the membranes reduced the turbidity by greater than 99.9%, as well as removing 51 ± 9% of organic species, with no drop in rejection performance after cleaning cycles. Although this presents a promising potential application, further study on the quality of the product water is required before it can be deemed suitable for implementation.

4. Conclusions

Building on previous work by the author and international membrane research community, a number of characterisation techniques were applied on used RO membranes subjected to extreme chlorine exposure in order to determine their suitability for reuse applications as UF-like membranes. In addition, this study focused on membrane storage methods, steps were taken to optimise the conversion pre-treatment methods, and the process was applied to a number of industrially used membranes. Permeability assessment of wet and dried membranes highlight the importance of proper storage conditions for RO membranes intended for direct reuse, as only partial performance recovery was achievable after drying. Tests were conducted to determine how different storage and pre-treatment conditions affected the extent of the conversion. Invariably, all membrane types tested benefited from pre-wetting, with performance increasing up to and potentially beyond 15 bar of applied pressure.

While it was shown that the membranes perform adequately, especially in terms of permeability and rejection, inconsistent performance across different membrane types, the requirement for high pressure pre-wetting and high chemical doses may limit the feasibility of large scale implementation. Each batch of membranes to be reused requires individual characterisation and assignment to a suitable application, and the unsanitary nature of the converted membranes possibly excludes their use in pharmaceutical and food processing applications. However, the supply of converted RO membranes as inexpensive UF membrane replacements for use in low cost humanitarian water treatment projects, low cost RO pre-treatment, or wastewater treatment operations is expected to benefit the industry. By utilising this alternative end of life option the volume of RO membranes sent to landfill will be reduced, limiting the associated social and environmental costs. Current and future work in this area is focused on the application of this optimised conversion process on whole RO membrane modules on a pilot scale, with the testing of specific applications of the resulting UF membranes. Additionally, a variety of tools including Life Cycle Assessment, will be used

to determine the financial and environmental sustainability of this process, when compared to alternative end of life disposal options.

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