REUSE OF REVERSE OSMOSIS DESALINATION MEMBRANES

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Abstract

Currently, membranes used in reverse osmosis (RO) desalination are generally disposed of via landfill. For economic and environmental reasons, other reuse, recycle and disposal options must be considered and investigated. This study aimed to assess the technical feasibility of removing the dense polyamide (PA) active layer of RO membranes, with the intent to reuse degraded RO into porous low pressure membranes. The study assessed the ability of three degrading solutions (NaOH, KMnO₄ and NaOCl) to remove the active layer, and used clean water filtration and salt rejection to compare the effect of different exposure intensities. The most promising results were found using NaOCl, membranes treated with at least 300,000 ppm.h of NaOCl presented an increased permeability to 175 ± 4 L.m⁻².h⁻¹.bar⁻¹ with less than 4% salt rejection. This shows that NaOCl performed significantly better than KMnO₄ as a degrading solution, with NaOH showing the least promising results. The fouling behaviour of the degraded RO membranes was also compared to commercially available ultrafiltration (UF) membranes, to which they displayed similar fouling characteristics and by using LC-OCD the molecular weight cut off (MWCO) of the reused membranes was estimated to be 5-10 kDa.
I. BACKGROUND

The rising demand of water for both potable and irrigation uses, as well as the shortages of water sources, has caused an increase in the use of reverse osmosis (RO) membranes around the world. The RO process uses a membrane consisting primarily of a dense active layer (mainly made from polyamide (PA)), a porous polysulfone (PSf) supporting layer, and a considerably thicker polyester base [1]. When RO is used in desalination plants, the raw input water is pre-treated in order to improve the performance of the process and to extend the life of the membranes, which generally have a lifespan of 3-5 years. Extending the operating life of these membranes has been the focus of much investigation. Ultimately however, once the module’s performance drops below the accepted level, they require replacement and the used membranes are disposed of with limited opportunities for reuse. There are obvious environmental and potential economic advantages to recycling or reusing the membranes.

[Figure 1: Estimated annual mass of membranes to be sent to Australian landfills.]

RO systems are becoming increasingly common. Every Australian state currently has, or is planning to build, at least one large scale sea water RO desalination plant. Figure 1 shows the projected tonnage of dry membrane modules to be disposed of in the coming years [2], from all applications of RO membranes. This projection assumes an average membrane lifespan of 5 years for all applications using a single pass design, and is based on the rough estimation that one hundred 8” RO modules are required per 1,000 m³/d (or MLD) of product water capacity. In reality, these numbers could be higher, as various plants use multi-pass systems, requiring a larger number of modules. The disposal of used membranes must also be considered in the context of increasing landfill disposal from Australia’s other industries. In Australia over 21 million tonnes of waste is placed into landfill each year, including more than 80,000 tonnes of polyethylene terephthalate (PET) water bottles and in excess of 300,000 tonnes of electronic waste [3]. It is crucial to investigate options to minimise the negative impacts of RO module disposal on the environment and to increase the lifecycle of the membrane elements.

Many options to extend the life cycle of the membranes need to be considered, including various forms of reuse and recycling [4]. In this context, reuse refers to using the membrane for the same function or a
new function with little or no treatment. Conversely, recycling is defined as breaking down the membrane and repurposing the individual components. End of life membrane modules are classified as general (non-putrescible) waste and are suitable for disposal in general landfill [5]. However, this is the least desirable outcome. With regards to recycling, many of the components of an RO module come under plastic categories that are already commonly recycled. For example, the polypropylene feed spacer, which constitutes 9% by weight of a 8” 13.5 kg RO module [6], is classified under international SPI resin identification code 5, and thus has the ability to be directly recycled. Polypropylene is commonly recycled into containers and packaging due to its strength and resistance to heat and chemicals. Depending on the type of polyester used, the permeate spacer, which makes up 5% by weight of the modules also has the potential to be directly recycled. The remaining plastic components of the membrane module fall under resin code 7 and cannot be recycled using general means, because they are either constructed from plastic blends, or they do not fall under any of the general plastic classification terms. If the components of the module are to be recycled individually a process, potentially automated, to disassemble and separate the plastics would be required.

Alternatively, the opportunity to directly reuse the modules in different applications with little or no treatment is one of the more favorable solutions that warrant investigation. Previous studies have explored the conversion of RO membranes to microfiltration (MF) and ultrafiltration (UF) membranes via a patented process involving chemically removing the active PA layer [7]. Other research, concluding that some aged RO membranes displayed nanofiltration behavior, has proposed that old RO membranes could potentially be used for lower grade wastewater treatment applications, seawater pre-treatment or selective demineralisation of brackish waters with little or no treatment [8].

To assess the viability of membrane reuse, the current study aims to investigate the feasibility of treating RO membranes with a variety of degrading solutions. This process aims to remove the active layer, which gives the RO membranes their characteristic selectivity, and thus creates a membrane with different properties. It is well documented that the active layer of RO membranes is extremely vulnerable to a variety of oxidising agents and this study exploits this disadvantage [9]. Despite the loss of salt-rejection ability, treated RO modules with exposed PSf porous supporting layers, could still be reused in systems requiring UF membranes (e.g pre-treatment system for new RO modules). Once the membranes have been treated, detailed characterization is required, so that their operation performance is understood and benchmarked against the membranes they are mimicking, before they can be used for a similar application.

II. MATERIALS AND METHODS

II.1 Active Layer Degradation

In this study new BW30FR membranes from DOW Chemicals were used, which are commonly used for brackish water treatment. Prior to the degradation experiment, each membrane was subjected to 2 h of compaction at 10 bar with Milli-Q water in a dead end stirred cell before the degradation process. The membrane samples were then passively (at atmospheric pressure) exposed to the degrading agent. The solutions used for treating the RO membranes were sodium hydroxide (NaOH), potassium permanganate (KMnO₄) and sodium hypochlorite (NaOCl) with exposure intensities ranging between 28,000 and 500,000 ppm.h. The concentration of the degrading agent was kept constant and the exposure time was varied to achieve an exposure intensity ranging between 28,000 and 500,000 ppm.h. For NaOCl, two concentrations were investigated, 6,250 and 62,500 ppm. These chemicals were chosen

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because of their known RO membrane vulnerabilities, and to compare the process to supporting literature. Following the degradation process, the membrane was flushed with Milli-Q water under pressure and the resultant permeability was measured. Following the permeability testing, a 2000 mg/L NaCl feed solution was used to assess the salt rejection, through the measurement of conductivity. All filtration experiments were conducted at 10 bar. Virgin BW30FR membranes have the permeability of 4 ± 0.2 L.m⁻².h⁻¹.bar⁻¹ and 99% measured salt rejection.

II.2 Reused membrane fouling assessment and comparison

A Millipore polyethersulfone (PES) 5kDa MWCO ultrafiltration membrane was used as a comparison to the degraded RO membranes. Prior to fouling, the degraded RO membranes and virgin UF membranes were tested for pure water permeability (PWP) and salt rejection using the method described above. The membranes were fouled with 10 mg/L bovine serum albumin (BSA) (Sigma-Aldrich) for 2 h at 2.5 bar in the stirred dead end cell. Although mainly composed of proteinaceous material, the BSA solution used in this study also contained a significant amount of smaller compounds such as building blocks and low molecular weight acids and neutrals. The PWP was tested again and then cleaning was carried out for 15 min using 0.5% NaOCl. Following the cleaning cycle, the PWP was measured once more to assess the effectiveness of the cleaning procedure. The cycle was repeated three times for each sample. Following accelerated fouling, permeate samples were analyses using LC-OCD, Model 8 manufactured by DOC-LABOR.

III. RESULTS AND DISCUSSION

III.1 Efficiency of various degrading agents

This study aimed to successfully remove the active PA layer of the membrane samples, through exposure to various oxidising agents. Two distinct concentrations of NaOCl were used to compare the effect of dosing a high concentration for short time and a lower concentration over an extended time, with both methods resulting in the membrane being subjected to the same degradation intensity (ppm.h).
The 62500 ppm NaOCl solution was shown to have a greater impact on permeability, reaching over 170 L.m\(^{-2}\).h\(^{-1}\).bar\(^{-1}\) at 187,500 ppm.h, while 6250 ppm NaOCl required over 300,000 ppm.h to achieve the same permeability. A similar difference can be seen in the effect on salt rejection, the high concentration NaOCl showing a more acute impact, with rejection dropping to 74% after being exposed for 30 min. Regardless of concentration, the membranes exposed to degradation intensities greater than 300,000 ppm.h of NaOCl produced a permeability of 175 ± 4 L.m\(^{-2}\).h\(^{-1}\).bar\(^{-1}\), all rejecting less than 4% of the NaCl in the test feedwater. This value of 175 L.m\(^{-2}\).h\(^{-1}\).bar\(^{-1}\) appears to be the end point, beyond which no further exposure to NaOCl increased the permeability. Figure 2 shows the error reported in the degradation intensity of NaOCl, which was calculated using the expected decline in free chlorine concentration over time. The degradation of chlorine has the potential to greatly effect results. Consequently, the testing was undertaken over a short period of time and in the absence of UV light to limit this phenomenon.

It has been concluded that, in terms of both permeability and salt rejection, NaOCl presents the most promising performance as degrading solution. This is illustrated by the higher permeability of the NaOCl-exposed RO membranes than that of both KMnO\(_4\) and NaOH, at every degradation intensity of exposure. Moreover, the salt rejection ability of the NaOCl-exposed membranes decreases more acutely than samples treated with the other two solutions. The effect of KMnO\(_4\) exposure on the membrane reflects interesting results, while the salt passage greatly increases the flux is not affected by the degrading process.

The results differ from the study conducted by Rodriguez et al. (2002), who found that KMnO\(_4\) most effectively degraded the RO membranes when compared to NaOCl and NaOH. However, their methodology used significantly lower degradation intensities (up to 12,000 ppm.h) and focused on variation in oxidant dose rather than intensity (ppm.h). Little information was provided regarding the hydraulic performances (i.e. permeability of the degraded membranes). The current study addresses both the salt passage and permeability of newly degraded membranes. Based on these more detailed results, it can be concluded that NaOCl appears more efficient in degrading the polyamide layer within comparative degradation intensities.

Previous studies have shown that passive exposure to oxidative agents does not affect RO membranes to the same degree as exposure under pressure [9]. However, these tests were conducted at low intensity (<15,000 ppm.h) when compared to this study. When considering a process to degrade large numbers of full size RO modules under chemical attack, it would be favourable to apply the process under passive conditions, this would reduce the energy cost of pressurising the system, as well as infrastructure.

**III.2 Degradation of used RO membranes**

In order to assess how the process of chemically degrading the membranes would apply to industry used modules, the degradation protocol was applied to TM700 (Toray Industries) brackish water RO membrane samples, which had been previously used for 3 to 4 years for brackish water treatment.
As shown in Figure 4, the permeability of the used RO membranes was consistently higher than that of virgin BW30FR membranes, after they were exposed to similar intensities of NaOCl. This can be attributed to the initial properties and condition of the different membrane types. The rate at which the permeability increased with changing concentration is most significant, both membrane types showed similar behaviour when subjected to NaOCl degradation, with the industry used membrane’s permeability increasing slightly faster with increasing degradation intensity, suggesting that the active layer of the TM700 membrane was more susceptible to degradation. Membranes of different makes and manufacturers will all respond differently to this degradation process. Furthermore, even similar membranes from various plants will be exposed to different conditions during their lifespan, as the feed quality and operating conditions vary for every process. Additionally, within the different plants, modules placed in various stages of the pressure vessel will be fouled and exposed unevenly. In light of these considerations, future research will address ways that the degrading protocol could be adjusted to compensate for variations in module use.

III.3 Benchmarking degraded RO membranes against UF

Work in the previous section indicated that the reused membranes displayed similar permeability and transmission characteristics of UF membranes. Based on the nature of the supporting material used in RO construction (known to be similar to UF structure) the concept of reusing the degraded RO modules in the place of UF membranes was introduced. For membranes to be successfully reused, benchmarking against currently employed technologies is required. The new surface of the converted membranes needs to be compared to existing commercially available UF membranes, with operating characteristics, such as fouling propensity and removal to be considered. In the preliminary testing of this benchmarking process, BW30FR membranes exposed to over 300,000 ppm.h of NaOCl, were tested through an accelerated fouling/cleaning cycle with BSA, alongside Millipore 5kDa UF membranes. The PES membrane was selected due to its low molecular weight cut off and availability. The BSA feed solution was chosen to create a simple fouling challenge test, from which material rejection could be assessed using LC-OCD, and MWCO of the newly degraded membranes could be estimated.
A possible limitation of this application is the potential to create a pitted and uneven surface that would be highly susceptible to fouling. Even if the initial specifications of the recycled membranes fit their new applications, the long term operation may be limited. Figure 5 shows how the membranes have responded to fouling and cleaning cycles. The reused RO membrane featured initial PWP of $171.8 \pm 4$ L.m$^{-2}$h$^{-1}$bar$^{-1}$ and after the first fouling cycle the permeability dropped to $21.3$ L.m$^{-2}$h$^{-1}$bar$^{-1}$. The tested UF membrane, started with a lower flux of $67.6$ L.m$^{-2}$h$^{-1}$bar$^{-1}$, however it experienced a similar drop in permeability of 81% (to $12.7$ L.m$^{-2}$h$^{-1}$bar$^{-1}$). After the first cleaning cycle, the UF and RO membranes recovered to 51 and 64% of their initial flux respectively, and both membranes experience relatively stable recovery from further fouling. According to the results shown, the degraded BW30FR membranes did not suffer from any catastrophic fouling, that would make the concept of reusing the membranes in this way unfeasible. Both membrane types were susceptible to irreversible fouling during the first cleaning cycle, however consecutive cycles reveal relative operational stability.

In previous work by Veza et al. [7], the converted membranes were used as pretreatment for RO for secondary waste water effluent, following cartridge filtration. While it was observed that the converted membranes underwent rapid fouling, measured by decay in permeability, it was reported that the membrane performance recovered well after chemical cleaning. A second method to reduce fouling was also investigated, the membranes were operated in a recirculation mode to increase the cross flow velocity. Research suggests this method effectively reduces fouling by avoiding deposition of solids.

Figure 5: Effect of accelerated fouling/cleaning cycles on degraded RO and commercial UF membranes
In order to better characterise the performance of the reused membranes, feed and permeates from the fouling cycles were collected and analysed using liquid chromatography organic carbon detection (LC-OCD), the spectrum obtained can be seen in Figure 6. The analysis showed that more than 99% of the proteins present in the feed were rejected by the UF and degraded RO membranes, while very little rejection of building blocks and low molecular weight acids was observed. As a result, the molecular weight cut off for the reused RO membrane was estimated to be between 5 and 10 kDa [10].

**IV. CONCLUSIONS**

With the increasing demand on water supplies, the number of large scale plants using RO technology is steadily increasing, with the resulting need to minimise the direct disposal of used membrane modules. This study investigated the technical feasibility of the conversion of used RO membranes to UF-like filters, by removing the active polyamide layer. RO membranes were treated with a variety of degrading agents, of which NaOCl proved to be the most successful, based on increase in permeability and salt transmission. In order for the process of reuse RO membranes to be widely accepted, the quality and performance of the degraded membranes need to be standardised and controlled, this may results in the process being changed for different types of RO membranes. The fouling behaviour of the reused membranes was assessed using short-term accelerated fouling/cleaning cycles. The results showed that the degraded RO membranes presented similar fouling characteristics to commercially available UF membranes. Using advanced analytical techniques, the MWCO of the reused membranes was estimated to be between 5 and 10 kDa. UF membrane modules are constructed differently to RO modules, including differing feed spacer width. It needs to be investigated whether these different physical properties could potentially lead to unwanted clogging of the repurposed membrane. The next stage in
this project is to apply the techniques discussed here to full-sized RO modules from industry desalination plants, and to investigate long-run fouling behaviour with real sea/brackish water feeds.

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VI. REFERENCES

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