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Application of robust MFI-type zeolite membrane for desalination of saline wastewater

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ABSTRACT

Zeolites are potentially a more robust desalination alternative as they are chemically stable and possess the essential properties needed to reject ions. This work proposes to use zeolite membranes for desalination of saline recycled wastewater for the possibility of avoiding the costly pre-treatment needed for polymeric reverse osmosis membranes. The MFI-type zeolite membrane was developed on a tubular α-alumina substrate by a combined rubbing and secondary hydrothermal growth method. The prepared membrane was characterised by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and single gas (He or N_2) permeation, and underwent desalination tests with saline wastewater under different conditions. When saline wastewater was fed at 7 MPa to the zeolite membrane it showed a salt rejection of 80% based on electrical conductivity (EC) and a flux of 4 $Lm^{-2}h^{-1}$.

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A_{254} (organics absorption at the wavelength of 254 nm measured by a HACH DR5000 spectrophotometer) removal exceeded 90%. Slightly lower salt removal and A_{254} results were observed when operating at a lower pressure of 3 MPa. During batch concentration runs on the saline wastewater, the EC of the feed water increased from the initial value of 1770 $\mu S.cm^{-1}$ to 3100 $\mu S.cm^{-1}$ over the 48 h test time which indicates that a 43% water recovery was achieved. EC reduction remained >70% and flux was maintained at around 2 $Lm^{-2}h^{-1}$ throughout the test period, indicating that the membrane resisted organic fouling. Chlorine stability studies showed that a long-term (7 days) strong hypochlorite clean did not significantly alter the flux or rejection confirming the chemical stability of zeolite membranes. Overall, the zeolite membrane showed excellent chemical resilience and produced a desalinated product suitable for reuse applications (e.g. irrigation, residential or industrial). Fluxes, however, need to be improved to be competitive with current polymeric membranes as do rejections for higher purity water applications.

Keywords: Desalination; Water recycling; Zeolite membrane; MFI; Seeded secondary growth

1. Introduction

Recycling of treated wastewater is a key approach in a sustainable water management portfolio both in Australia and in other parts of the world to minimise the growing water demand in a water scarce environment [1-3]. Secondary treated wastewater could possibly be reused for various purposes such as agricultural irrigation, landscape irrigation, industrial recycling, stream flow augmentation, and non-potable reuse. Prior to this reuse, the refractory organic pollutants and high salt concentrations in secondary wastewater must be removed, which presents a challenge to water recycling practice [4, 5]. Therefore various advanced treatment techniques are needed to address these challenges.

The application of membrane technology in reuse of the municipal wastewater effluent has dramatically increased over the past decade. However, polymer membranes have fouling problems [6, 7] and will also degrade when exposed to extreme acidic, alkaline [8], or oxidising environments [9]. Apart from these, the lifespan of the polymer membranes will also be shortened when used in a harsher environment with more abrasive particles due to their low abrasion-resistant ability [10, 11]. Desalination of saline recycled water is currently performed using polymer reverse osmosis (RO) membranes, which imposes strict pre-treatment requirements such as coagulation and/or micro/ultrafiltration (MF/UF). Chloramination, acid cleaning and biocides are also used to maintain performance of the chemically sensitivity RO membranes. Despite the strict pre-treatment requirements, polymer RO membranes eventually need to be replaced around every 5–7 years due to damage caused either by foulants or the chemicals used for cleaning [12]. Cleaning chemicals and membrane replacement account for 60% of the operating cost for the pre-treatment system, or around 30% of the total operating costs for combined pre-treatment and desalination [13]. Therefore, research and development of more robust alternative membrane materials such as ceramic membranes could potentially eliminate pre-treatment and biological fouling (biofouling)/cleaning issues, thus reducing the operating costs.

In addition to the strict pre-treatment requirements, polymer RO membranes are known to be very susceptible to chlorine [14-17], yet this chemical is widely used in water treatment for biofouling control. It cannot be used for cleaning RO membranes, as even a few parts per million of chlorine present in the feed water could significantly degrade the membrane material [18]. Therefore, many studies have been carried out to develop chlorine-resistant RO membranes [19, 20]. Despite the positive progress, developing robust RO membranes still remains a challenge. Further studies are needed to continuously improve RO membrane performance (e.g. chlorine tolerance, fouling resistance and abrasion resistance) which contributes towards the reliable long term operation of desalination processes.

Ceramic membranes made from zeolites have been studied for gas and liquid separations [21-23], and membrane reactors [24] due to their high separation performance, good catalytic activity, high thermal, chemical and mechanical stability as well as chemical and solvent resistance [25, 26]. There have been some studies to date applying zeolite membranes in the application of desalination [27-36]. These studies have shown that zeolite membranes are promising candidates for desalination of saline water including seawater, as they possess the nanoporous structure required to remove ions from aqueous saline solutions. Therefore, they may be used as an alternative to polymeric membranes for treatment of complex wastewater containing organic solvents and radioactive elements [27, 31].

To be suitable to remove salt ions from aqueous solutions, the zeolite pore size and intercrystalline interconnections should be well below the size of hydrated salt ions (e.g. Na^+

0.716 nm, Cl^- 0.664 nm, K^+ 0.662 nm [37]). The MFI-type zeolite has orthorhombic crystal symmetry with nearly cylindrical, 10-member ring channels [38]. The aperture size of the MFI-type zeolite is approximately 0.56 nm [29], which theoretically meets the criteria as mentioned above for selective separation of water (kinetic diameter 0.276 nm [37]) from hydrated salt ions. Several research groups have explored the possibility of using MFI-type zeolite membranes for desalination [27-31, 34-36, 39]. It was found that performance testing of MFI-type zeolite membranes working in RO are able to deliver high ion or salt rejections; for example, a high rejection (>93%) was achieved for Ca^{2+}, Mg^{2+} and Na^+ from a 0.3wt% seawater solution at 700 kPa [35], and Na^+ rejection was measured at 99.4% at 2.76 MPa for 0.1 M NaCl solution (5,840 mg/L, or approximately 9,150 µS.cm^{-1}) [39]. Recently, researchers have also attempted to treat laboratory prepared water using MFI-type zeolite membranes [39, 40]. These studies showed that MFI-type zeolite membranes had great potential for separation of dissolved organics from aqueous solution, as an example, an organic rejection of 99.5% was achieved for 100 ppm toluene with a water flux of 0.03 $Lm^{-2}h^{-1}$at an operation pressure of 2.76 MPa [39]. However, little work has been carried out on performance of MFI-type zeolite membranes for desalination of commercial solutions containing multiple inorganic and organic components such as saline wastewater. Further, the capability to survive chlorine cleaning has not been explored.

2. Experimental and methods

2.1. Materials

1M tetra-propyl ammonium hydroxide (TPAOH) solution, sodium hydroxide pellets (NaOH, 99.99%), fumed silica (SiO_2, 99.98%, particle size 0.014 µm, surface area 200±25 m^2g^{-1}) and tetraethyl orthosilicate (TEOS) (98%) used for zeolite seeds and membrane preparation were purchased from Aldrich. All these chemicals were used as received without further purification. The porous α-Al_2O_3 tubular support (99.7% Al_2O_3, ~31vol% porosity, external diameter 15 mm, internal diameter 10 mm, length 25 mm, ~0.58 µm nominal pore size) used for the current work was supplied by Chosun Refractories Co. Ltd, Korea.

The water source used for this study was saline wastewater collected from a water treatment plant in Melbourne, Australia. Typical characteristics of the water sample are shown in Table 1. The wastewater was collected after ultraviolet (UV) and chlorine disinfection, just prior to being sent for reuse by local industries and residents. As this water is also the feed to a newly constructed desalination plant which uses polymer membrane ultrafiltration (UF) and RO, it serves as a suitable water to be instead desalinated without pre-treatment by a more robust zeolite membrane and is thus to feed to the tests presented here.

Table 1 Typical characteristics of saline wastewater sample

Parameter	**Value**
pH	7.6
EC, μS.cm^{-1}	1770
True colour, Pt-Co Units	25
$A_{254,}$ cm^{-1}	0.16
TOC (total organic carbon), mgL^{-1}	12.3

2.2. Membrane preparation

The MFI-type zeolite membrane was coated on the porous α-Al_2O_3 tubular support by a secondary growth technique, which involved depositing zeolite seeds (silicalite) on the support using a rubbing method [41, 42] followed by growth of the membrane under hydrothermal conditions. The hydrothermal secondary growth was carried out in a growth solution of 2 mL of 1M TPAOH, 2 mL of TEOS and 36 mL deionised water at 180 °C for 16 h. After growth, the membrane was washed in deionised water to remove loose precipitate and was then calcined at 500 °C for 4 h. Prior to membrane preparation, the bare α-Al_2O_3 tube was tested under high pressure up to 10 MPa, confirming that the ceramic tube used in this study for membrane preparation can withstand the desalination test system desired pressure (e.g., 7 MPa).

The silicalite MFI zeolite seed powders used for seed-deposition were prepared by calcining the silicalite suspension at 525 °C for 6 h with a temperature increase/decrease rate of 1 °C.min^{-1} to remove the organic template from the zeolite framework. The silicalite suspension was synthesised from a solution of 43 mL of 1M TPAOH, 0.6 g NaOH and 8.5 g fumed silica using a hydrothermal process [30] at 180 °C for 8 h. The hydrothermal synthesised suspension was thoroughly washed with deionised water by repeating centrifugation and re-dispersion in deionised water four times prior to the calcination.

2.3. Membrane desalination

The desalination performance of the prepared zeolite membrane for saline recycled wastewater was evaluated in the desalination test system used in our previous work [34]. The membrane was installed into the stainless steel membrane housing, and the feed solution (deionised water or recycled water) was fed at a flow rate of 5 mL.min^{-1} by a high pressure piston pump (Series 1, LabAlliance, USA) with an applied gauge pressure of up to 7 MPa. The desalination experiments were conducted in a cross-flow setup with the water being fed under pressure on the outside and permeating to the inside of the membrane.

2.4. Water sample analysis

The desalination performance was determined by the measured electrical conductivity (EC) values and cation concentrations of the water samples. EC of the recycled water feed and collected permeate samples were determined with a portable conductivity meter (Sension 156, HACH). Cation analysis was performed by inductively coupled plasma-optical emission spectrometry (ICP-OES) (Shimadzu ICPE-9000). True colour (Pt-Co units) and A_{254} (cm^{-1}) were measured by a spectrophotometer (HACH DR5000, USA) using the standard methods provided by HACH. TOC was determined by a TOC-Vcsh TOC analyser (Shimadzu, Japan). High performance size exclusion chromatography (HPSEC) was used to determine the molecular weight distributions of the water samples. HPSEC analysis was performed with a photodiode array (PDA) using a TSK gel column (G3000 SW, C-No. SW 3600482) at room temperature with a phosphate buffer (10 mM KH_2PO_4+10 mM Na_2HPO_4, 0.04M, pH 6.8) as the mobile phase. The column was operated with a flow rate of 0.5 mL.min^{-1} and a 50 µL injection volume. Polystyrene sulphonate (PSS) molecular weight standards of 3,420, 4,600, 6,200, 15,650 and 39,000 Daltons were used to calibrate the LC column. The absorbance results for HPSEC are reported as UV_{254} and UV_{210} for absorbance at 254 and 210 nm.

2.5. Characterisation

The MFI-type zeolite membrane was characterised by SEM, XPS and single gas (He or N_2) permeation to determine any changes in membrane structure, morphology and surface elements after desalination testing with saline recycled wastewater under different conditions. Prior to characterisation, the desalination tested membrane underwent deionised water permeation to remove weakly adsorbed material (including ions).

SEM images were obtained from the secondary electron detector of a CamScan MX2500 microscope (CamScan Optics, Cambridge, UK) using a 10 kV electron beam with a working distance of 2.2 mm.

XPS analysis of the samples was conducted in an ultra-high vacuum (UHV) system built by SPECS (Berlin, Germany) with a base pressure of 10^{-10} torr. A non-monochromatic X-ray source (Mg Kα – 1253.6eV) was used to generate Kα radiation. A Phobios 100 energy analyser built by SPECS was used to count the spectra of electrons emitted from the membrane surface. The angle between the X-Ray source radiation and the analyser was 54°, the x-ray source was run with a power of 100W, voltage of 12keV and the spectra of electrons were collected with a pass energy of 10eV. High resolution XP spectra were fitted with combined Gaussian-Lorentzian components using a Shirley background correction.

Gas permeation was carried out using a simple membrane test system as described in our previous study [34] to evaluate the intactness of the synthesised zeolite membrane. The membrane was installed into the same membrane housing used for desalination testing. To release adsorbed water (water molecules can occupy the tight micropore spaces of the zeolite structure), the membrane was oven dried at 100 °C in a temperature control unit prior to gas permeation testing. Permeation of either He or N_2 was carried out at 100 °C by feeding the gas at 100 kPa to the film-side of the membrane. Any pressure decay that occurred during the permeation test was monitored by a TPI 665 digital manometer (Test Products International, Inc. USA). The pressure was recorded by a computer with TPI 665 Data Logger software. Permeation was calculated by converting the pressure decay to membrane permeance.

3. Results and discussion

3.1. Desalination performance under different applied pressures

Figure 1 shows the reduction of EC and A_{254}, and flux on the prepared MFI-type zeolite membrane fed with saline recycled wastewater under different applied pressures (1–7 MPa). Both EC reduction and flux increased with an increase of the applied pressure. There was an increase in EC reduction when the applied pressure was increased from 1 MPa (~56%) to 3 MPa (~73%). However further increase to the applied pressure only provided a small increase in EC reduction. The flux increased an order of magnitude when the applied pressure was increased from 1 MPa to 7 MPa. The results appear to follow the effect related to change in driving pressure after overcoming the osmotic pressure [34]. The membrane also achieved a high reduction in A_{254} (>90%) under all the pressures tested except for 1 MPa (~89%). A_{254} is a parameter indicating the quantity of unsaturated bonds (double bonds or triple bonds) contained in organic compounds. A higher quantity of unsaturated bonds leads to an increase in the A_{254} absorbance. The A_{254} measurement in the feed and permeate samples is an effective parameter to indicate the membrane performance on the removal of organics. The A_{254} results obtained in this study suggest a good ability for organic rejection, and overall improvement in the aesthetics (e.g. colour) of the water due to the removal of organics containing double bonds.

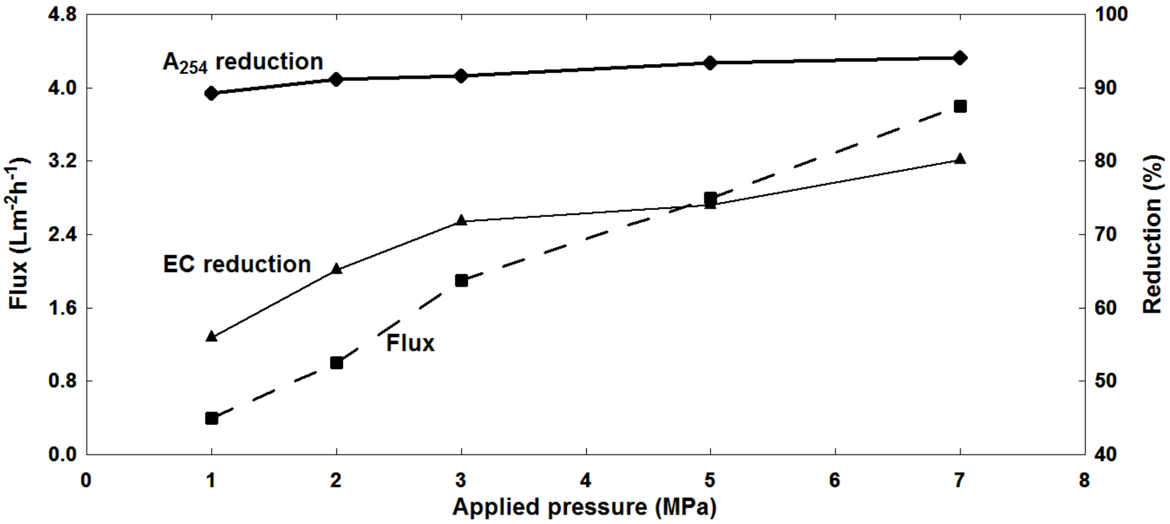


Fig.1. Reduction of EC and A_{254}, and flux under different applied pressures (1–7 MPa) and 21 °C when fed with saline recycled wastewater.

The rejection of cations calculated from the ICP-OES results is shown in Figure 2. The results confirmed that higher applied pressure (up to 7 MPa) gave higher ion rejection. The membrane achieved a high rejection (~90% or above) for Ca^{2+} and Mg^{2+}, and a good rejection (>70%) for K^+ and Na^+ when the operating pressure was applied at 3 MPa or above. Based on these results, it appears the membrane works more like a nanofiltration membrane which permeates small monovalent ions in preference to multivalent ones.

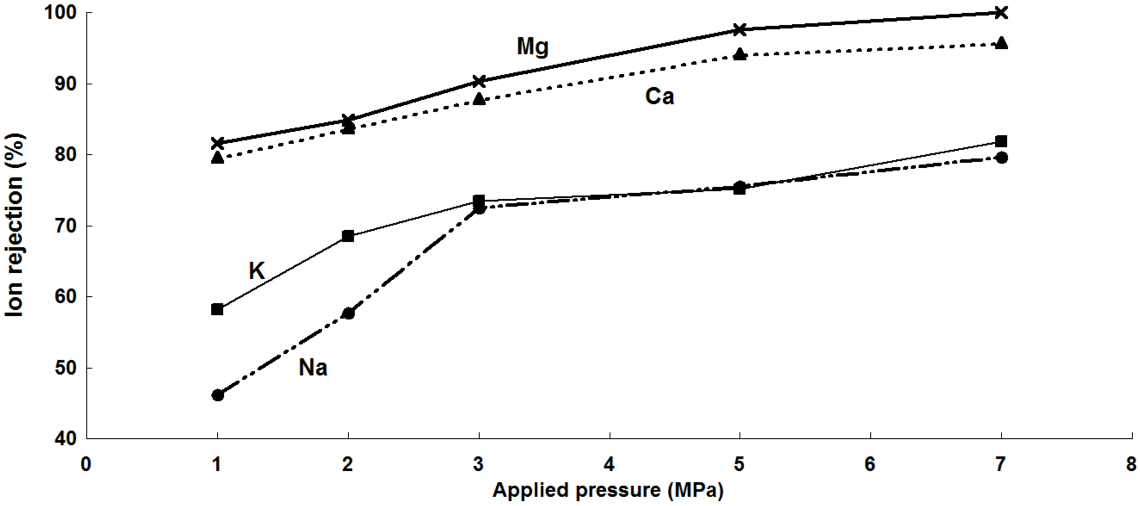
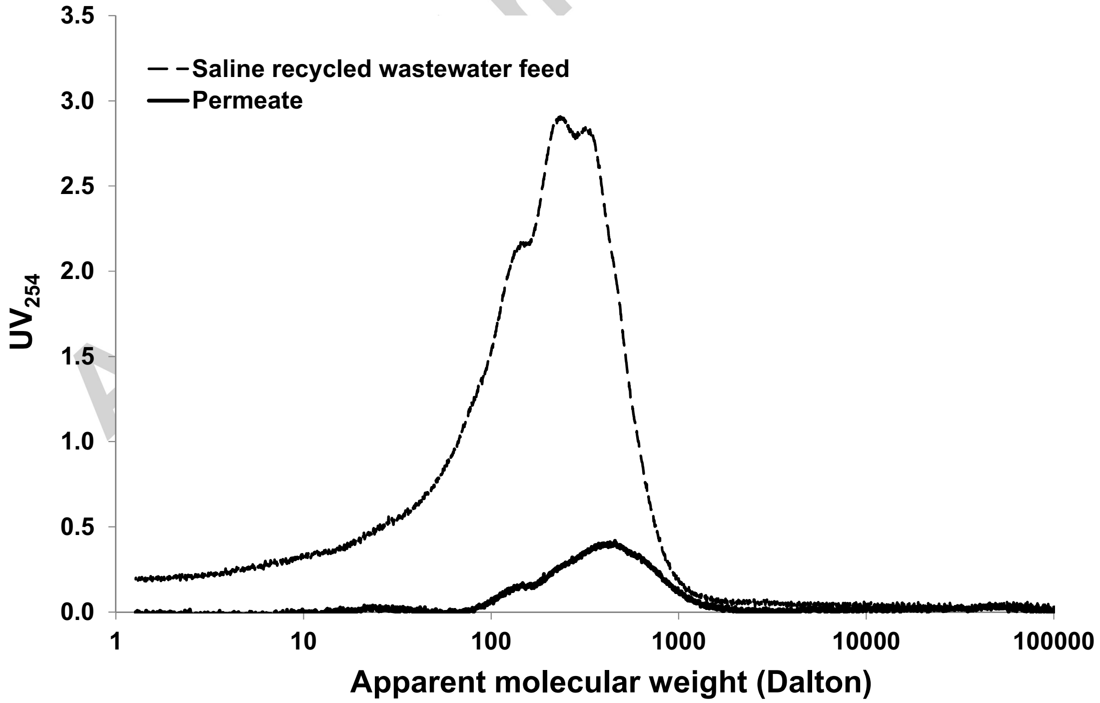


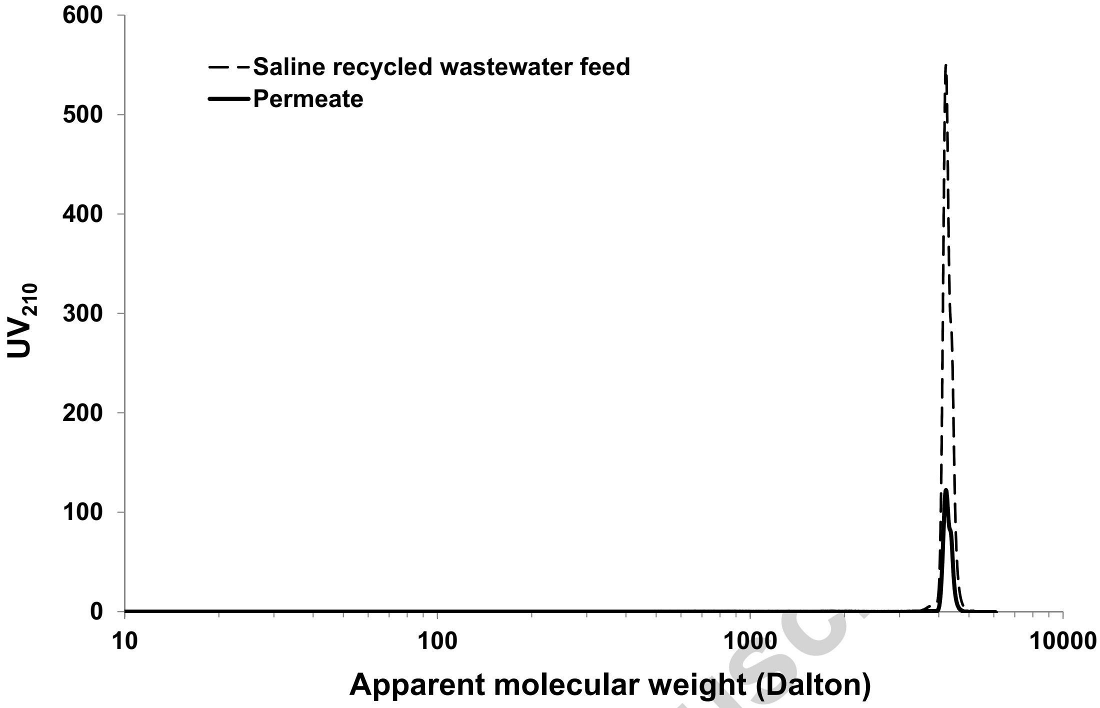
Fig.2. Ion rejection versus applied pressure (1–7 MPa) fed with saline recycled wastewater at 21 °C.

TOC and HPSEC measurements were also carried out on the water samples to determine the membrane's ability for removal of organic compounds. The results from TOC measurements showed that the membrane achieved a TOC reduction of ~90% at an applied pressure of 3 MPa and room temperature (21 °C). This is in good agreement with the A_{254} (>90%) result as shown in Figure 1.

Figure 3 compares HPSEC UV_{254} and UV_{210} chromatograms of feed water and the permeate sample obtained from the desalination test (Fig. 1) at an applied pressure of 3 MPa and 21 °C. The UV absorbance at 254 nm (UV_{254}, Fig. 3a) shows the aromatic substances (unsaturated bonds) [43], while the absorbance at UV 210 nm (UV_{210}, Fig. 3b) detects amine groups as well as carboxylic acids and can therefore detect proteins [44]. It was found that the majority of aromatic compounds present in both recycled wastewater feed and permeate samples have a range of molecular weights from ~100–1000 Daltons (Fig. 3a). However, UV_{254} measured for the permeate sample was significantly smaller than that of the feed water (saline recycled wastewater), indicating that a large proportion of aromatic substances present in feed water has been removed by the membrane under the testing conditions (3 MPa and 21 °C). The molecular weights of the majority of UV_{210} substances in the water samples ranged from ~4000–5000 Daltons (Fig. 3b), consistent with these compounds being protein-like. Similar to the UV_{254} results, the permeate sample showed a significantly low value of UV_{210} when compared to that of the feed water, indicating that a large proportion of the protein-like compounds present in the feed were also removed by the membrane under the testing conditions mentioned above. The HPSEC results are in agreement with the TOC results.



(a) UV_{254}



(b) UV_{210}

Fig.3. HPSEC UV_{254} (a) and UV_{210} (b) chromatograms of saline recycled wastewater and the permeate sample from desalination test under an applied pressure of 3 MPa and 21 °C

Although the TOC and HPSEC results showed that the majority of organic compounds present in the feed water were removed by the zeolite membrane under the testing conditions (3 MPa and 21 °C), some aromatic compounds (molecular weights up to 1000 Daltons) and protein-like substances with a narrow spread of molecular weights (~4000–5000 Daltons) still remained in the permeate (Fig. 3). This indicates that diffusion might have occurred in the defects of the membrane (grain boundaries). It is known that the typical range of molecular weight cut off (MWCO) is <100 Daltons for reverse osmosis (RO) membranes (pore size <1 nm) and 200–1000 Daltons for nanofiltration membranes (pore size ~1–10 nm) [45].

It is well known that MFI-type zeolites have a typical intrinsic pore size of 0.54–0.56 nm size [29, 38, 46, 47]; but smaller intrinsic pores (e.g. ~0.3 nm) and intracrystalline pores of 1.1–1.2 nm have also been measured by positron annihilation lifetime spectroscopy (PALS) which was attributed to ions occupying pore spaces [48, 49]. Micropores of size between 1 nm and 2.5 nm have been previously detected in silicalite-1 by n-hexane porosimetry [50]. In general, to achieve excellent salt rejection and organics removal, defect free zeolite membranes are necessary and diffusion should ideally occur only through the regular intra-crystalline pores (~0.56 nm) within the zeolite cages. However, preparation of defect free thin films is challenging [51]. Therefore, in reality, the permeation properties will often be modified due to the existence of inter-crystalline defect porosity caused by insufficient intergrowth of crystals, thermal removal of the template, or the complete de-watering of the materials [52, 53]. Also the intra-crystalline and inter-crystalline porosity of the zeolite membrane could change due to the interactions between zeolite and ions present in the feed solution (e.g. increasing in pore sizes due to ion adsorption and ion exchange), and this change could have a significant impact on diffusion properties of the membrane [48, 49]. Li et al. [28] have proposed that different mechanisms control the transport of ion and water molecules through the intracrystal zeolite channels and the intercrystal pores. Ion rejection by the zeolitic channel is controlled by a size exclusion effect on the large hydrated ions. Ion separation through the intercrystal micropores is caused by the strong interaction between the ion and the charged double layers. The ion-double layer interaction restricts ion diffusion in the microporous space.

3.2. Performance during increasing water recovery (batch concentration)

In desalination plants, the membranes must also operate at high water recoveries which results in rising concentration of salts along the brine side of the membrane train. The results for increasing concentration of the same feed obtained at 3 MPa are shown in Figures 4 and 5. It was found that the EC of the feed water increased from 1770 μS.cm^{-1} to 3100 μS.cm^{-1} over the 48 h test time. However, the overall EC reduction remained high (>70%) throughout the test period (Fig. 4). Similar to EC, A_{254} of the feed water at the end of 48 h testing (0.33 cm^{-1}) was double the initial feed water (0.16 cm^{-1}), indicating an accumulation of organics in the reject stream. However, the flux remained almost unchanged at ~2 Lm^{-2}h^{-1} over 48 h test period (Fig. 5), suggesting that the zeolite membrane was able to perform without pore blocking from organic or inorganic species in the water. The EC and A_{254}

reductions, and flux from batch concentration testing were similar to those obtained from initial performance test under the same conditions (Section 3.1). The overall water recovery over 48 h test period was estimated to be 43% based on the volume of the collected permeate and the initial volume of the saline recycled feed water. The fluxes here (specific fluxes were estimated to be 6.8 ×10^{-4} $Lm^{-2}h^{-1}kPa^{-1}$ based on the calculation in the previous study [35]), however, are lower than that expected for polymer RO membranes on the same wastewater, where fluxes of 18 $Lm^{-2}h^{-1}$ at only 1 MPa (specific fluxes were estimated to be 196 ×10^{-4} $Lm^{-2}h^{-1}kPa^{-1}$ using the same calculation [35]) are recorded using BW30 RO membranes from DOW FILMTEC. Flux improvements are therefore needed in order to achieve comparable productivities to the state-of-the-art polymer membranes. While the fluxes achieved in this study are lower than that recorded for BW30 RO membranes on the same wastewater, we acknowledge that the MFI zeolite membrane synthesised in this study (thickness 9.8 μm, Fig. 7b) are much thicker than RO membranes (0.2 μm) from DOW FILMTEC [54]. Membrane resistance to water transport is proportional to the dense skin thickness. As a result, water fluxes on polymer membranes are much higher than those through zeolite membranes.

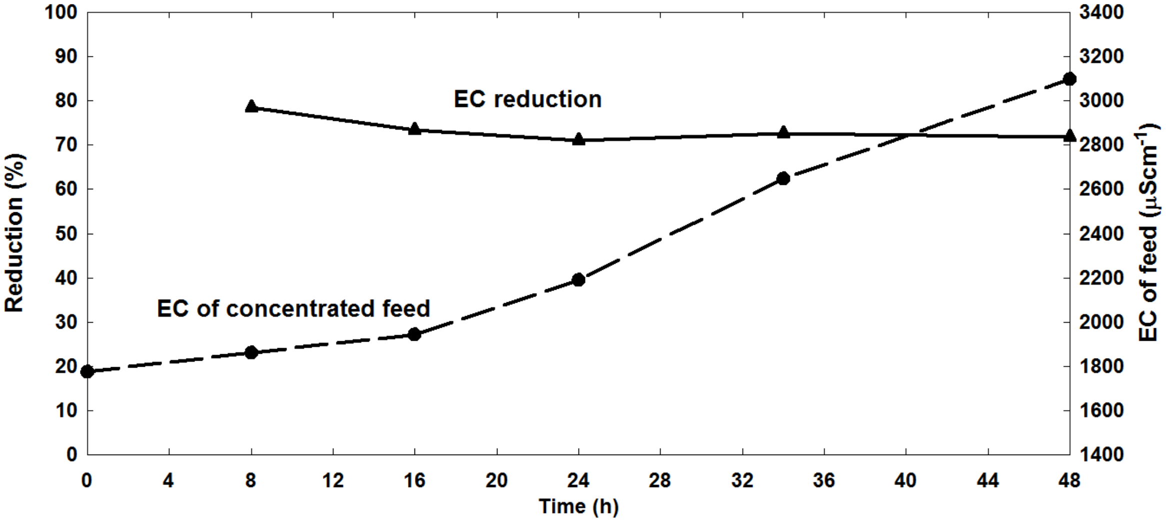


Fig.4. Effect of EC of concentrated feed on EC reduction. Recycled wastewater fed at 3 MPa and 21 °C.

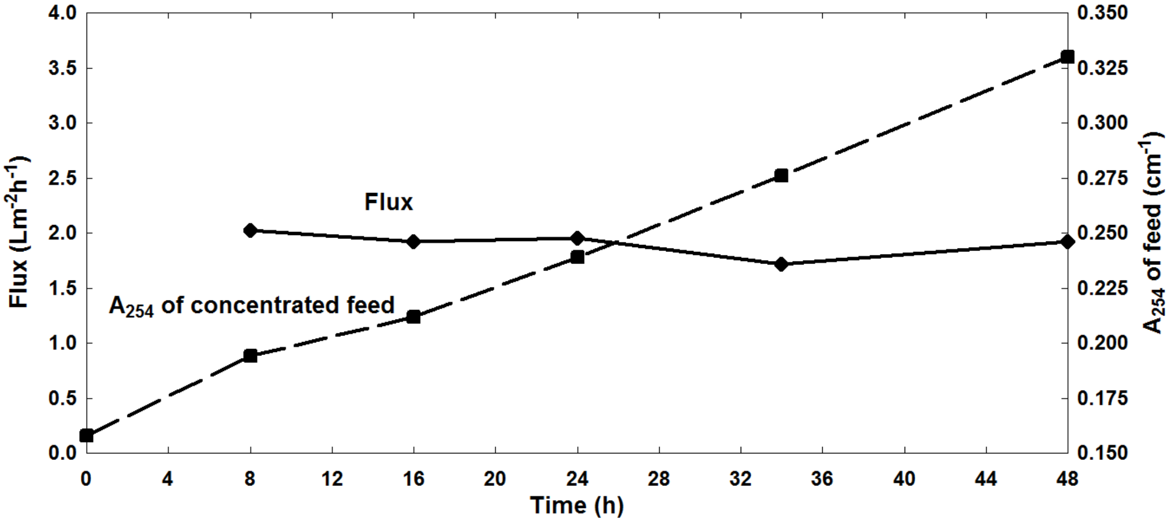


Fig. 5. Effect of A_{254} of concentrated feed on flux. Recycled wastewater fed at 3 MPa and 21 °C.

Overall, the prepared MFI-type zeolite membrane achieved a good removal for both ions and organic compounds at an applied pressure of 3 MPa and room temperature tested up to an overall water recovery of 43%. The achieved ion rejections are possibly not high enough for seawater desalination when compared to commercial polymer membranes which can achieve up to 99.8% salt rejection. However, the average EC value of the permeate was sufficiently low, at ~500 µS.cm^{-1}, making it suitable for potential reuse applications (e.g. irrigation water). Such plants can operate up to 80% water recovery, so future testing on zeolite membranes for this application should attempt to achieve at least an equivalent recovery.

3.3. Effect of long-term hypochlorite clean on desalination performance

A recent autopsy study carried out by Chesters et al. [10] on 99 seawater RO membranes from 13 countries showed that biofouling is the primary cause of RO membrane failure. As mentioned earlier in Section 1, chlorine is a useful chemical for controlling biofouling in water treatment applications, but is an oxidant to commercial polymer RO membranes and must be strictly avoided. Therefore, a test was conducted to see if the zeolite membrane can tolerate concentrated chlorine for possible biofouling control or cleaning applications. Following the batch concentration test (Section 3.2), the desalination testing system was flushed with deionised water and the membrane was retested with fresh saline recycled wastewater at an applied pressure of 3 MPa and 21 °C. The reduction of EC and A_{254}, and water flux obtained for this test are shown as "Before hypochlorite clean" in Table 3. After finishing this test, the membrane was left in the same feed water for 7 days and then in 1000 ppm hypochlorite solution for another 7 days (168,000 ppm.h). After this exposure period, the system was flushed with deionised water, and then underwent desalination testing again with the same saline recycled wastewater under the same conditions as above. The results from this test are shown as "After hypochlorite clean" in Table 3. As can be seen from Table 3, there was almost no change in EC and A_{254} reductions, and only a slightly increase in water flux before and after hypochlorite clean, indicating that long-term (7 days) hypochlorite cleaning did not reveal any major impact to the membrane's desalination performance. The reduction of EC and A_{254} from this test was also similar to those obtained from the initial performance test (Section 3.1) and batch concentration testing (Section 3.2) under the same conditions, indicating that the membrane has the good stability on desalination performance.

Table 3 Reduction of EC and A_{254}, and water flux before and after long-term hypochlorite clean, fed with saline recycled wastewater at an applied pressure of 3 MPa and room temperature (21 °C).

Parameter	Before hypochlorite clean	After hypochlorite clean	Change (%)
EC reduction (%)	68.5	70.1	+2.3
A_{254} reduction (%)	88.9	86.4	-2.8
Flux ($Lm^{-2}h^{-1}$)	2.3	2.5	+8.7

Figure 6 compares the rejection of major cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) obtained from the initial performance test and after a total of 250 h testing and 168,000 ppm.h chlorine exposure under the same conditions (3 MPa and 21 °C). No significant difference in ion rejection was observed between the initial performance test and after long-term strong hypochlorite clean. The membrane retained its high rejections for Mg^{2+} (90%) and Ca^{2+} (82%), and good rejections for Na^+ (70%) and K^+ (78%) at an applied pressure of 3 MPa and 21 °C after long-term hypochlorite cleaning. These results confirmed that the membrane can withstand a long-term (7 days) strong hypochlorite (1000 ppm) cleaning (168,000 ppm.h) without any loss of ion rejection. By comparison, while some other polyamide RO membranes have essentially zero chlorine tolerance, the FILMTEC FT30 membrane with superior chlorine tolerance from DOW can only withstand approximately 200–1000 hours of exposure to 1 ppm of free chlorine (200–1000 ppm.h tolerance) in its operational lifetime [55].

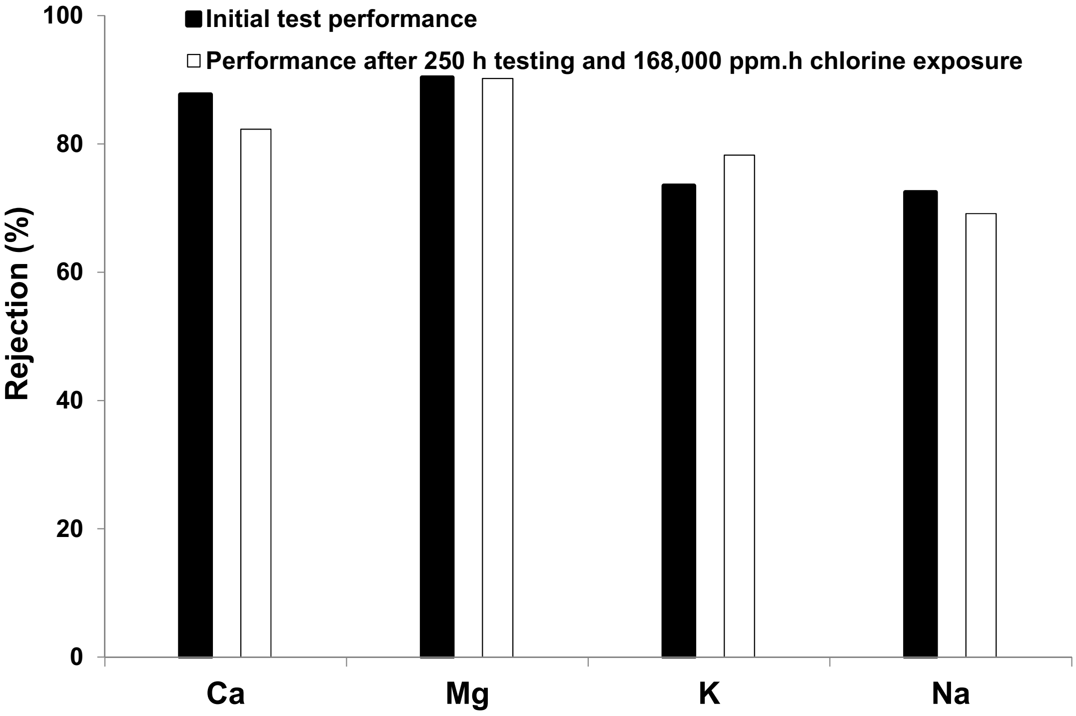
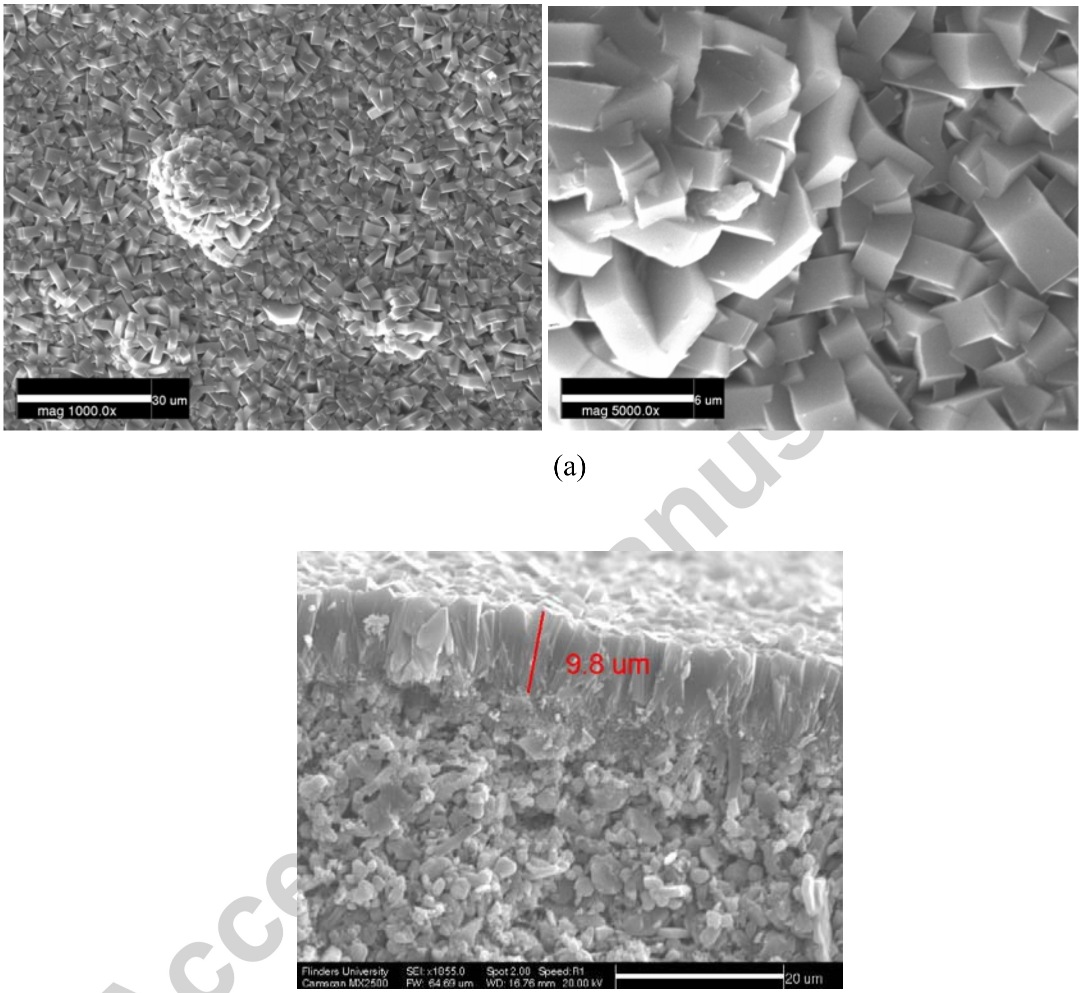


Fig.6. Comparison of ion rejections on the membrane performance from the initial test and after 250 h testing and long-term hypochlorite clean (168,000 ppm.h), fed with saline recycled wastewater at an applied pressure of 3 MPa and room temperature (21 °C).

3.4. SEM

Figure 7 shows the SEM images of the surface and cross-section of the MFI-type zeolite membrane after 250 h desalination testing with the saline recycled wastewater. The SEM images (Fig. 7a) of the zeolite membrane surface showed typical randomly orientated MFI-type zeolite crystals [34], indicating that a zeolite membrane layer was formed on the surface of the Al_2O_3 support. Most of the zeolite crystals laid disorderly on the surface of the α-Al_2O_3 support. The thickness of the zeolite membrane was measured to be ~9.8 μm (Fig. 7b). When compared to the SEM image [34] on the surface of the untested zeolite membrane prepared by the same procedures used for the this study, the SEM measurements on the membrane surface (Fig. 7a) also showed that macrostructure of the zeolite membrane remained intact after desalination testing with the saline recycled wastewater.



(a)

(b)

Fig.7. SEM images on (a) the surface and (b) cross-section of the desalination tested MFI-type zeolite membrane.

3.5. XPS

Elemental surface analysis was undertaken using XPS on the bare α-Al_2O_3 substrate, as well as the original and desalination tested MFI-type zeolite membrane. The XPS was able to show elemental changes after exposure to the saline recycled wastewater. It should be noted that the membrane was subjected to deionised water permeation after testing with the saline recycled wastewater. The detection therefore of the waterborne ions after saline recycled wastewater and deionised water permeation is a good indicator that the ions are tightly bound to the zeolite surface due to strong interactions between the zeolite and ions present in the feed solution as was also observed in our previous studies [35, 48, 49].

Table 4 shows the XPS measured atomic percentage (at%) of the elements corresponding to the zeolite material (e.g. Si, O) and major elements (e.g. Na, K, Ca, Mg, Cl) present in the saline recycled wastewater used in this study. Comparing the saline recycled wastewater exposed membrane, an overall reduction in the zeolite elemental concentrations of Si and O is observed. A similar trend was also observed in the previous study on the seawater exposed membrane by energy-dispersive X-ray spectroscopy (EDS) mapping [35]. There was a slight increase in Ca (a major cation present in the saline recycled wastewater) after testing with the saline recycled wastewater (Table 4). A very small amount of Na (major cation present in the saline recycled wastewater) was also detected on the saline recycled wastewater exposed membrane surface (Table 4). These changes suggested that interactions have occurred between the zeolite material and the waterborne cations during exposure of the membrane to the saline recycled wastewater. Mg, K and Cl (other major ions present in the saline recycled wastewater used in this study) were not detected on the zeolite membrane. Considering the slight response overall, the membrane did not significantly adsorb ions during exposure to the saline recycled wastewater, or the adsorbed ions concentrations are below the XPS detection limits of 0.1 at%. Alternatively the ions may be adsorbed within the membrane structure and are therefore not able to be detected using XPS which has a depth resolution of approximately 10 nm [56]. The analyses of the zeolite membrane did not penetrate the entire thickness of the zeolite membrane, as no Al present in the substrate was detected.

Table 4 XPS analysis of elements on the surface of the bare α-Al_2O_3 substrate (fresh material), the zeolite membrane before and after 250 h desalination test with the saline recycled wastewater

Element	Bare tube (at%)	Membrane before desalination (at%)	Membrane after desalination (at%)
C 1s	54.8	22.9	30.6
O 1s	18.3	58.2	53.2
Si 2p	3.0	18.8	15.4
Al 2p	15.9	-	-
Ca 2p	1.6	0.1	0.3
Mg 2p	-	-	-
K 1s	-	-	-
Na 2s	3.2	-	<0.5
Cl 2p	0.8	-	-
N 1s	2.4	-	-
Total	100	100	100

3.6. Gas permeation

The permeation of single gases (He or N_2) measured for the original and saline recycled wastewater tested (a total of 250 h testing and 168,000 ppm.h chlorine exposure) zeolite membrane is shown in Table 5. The gas permeation results for the bare α-Al_2O_3 support are also included in Table 5 for comparison.

The permeance of He and N_2 measured for the original zeolite membrane was significantly smaller than that of the bare Al_2O_3 substrate, confirming the formation of a rate determining layer on the α-Al_2O_3 support, which is confirmed to be made up of zeolite crystallites as shown by SEM (Fig. 7). The MFI zeolite membrane prepared in this study showed a similar level of He permeance to that reported in literature [57].

Table 5 He and N_2 gas permeation testing on the α-Al_2O_3 support and zeolite membrane at 100 °C before and after 250 h desalination testing with saline recycled wastewater

Membrane condition	Permeance of He ($\times 10^{-8}$ mol$m^{-2}s^{-1}Pa^{-1}$)	Permeance of N_2 ($\times 10^{-8}$ mol$m^{-2}s^{-1}Pa^{-1}$)	He/N_2
Bare α-Al_2O_3 support	285	187	1.5
Original	39.5	37.1	1.1
After desalination	4.6	2.8	1.6

After 250 h desalination testing with saline recycled wastewater, the gas permeation decreased by an order of magnitude for both gases, but slightly more for the larger N_2 molecule (noted by the increase in He/N_2 permselectivity). While the membrane remained intact, which was also observed in the SEM study, the overall decrease in permeation implies a closure of the porous structure. A similar effect from desalination of seawater on zeolite membrane discs has been observed where gas permeance greatly reduced after desalination, and He/N_2 selectivity increased [35]. It was concluded that adsorbed cations in the zeolite block gas diffusion in the dry testing condition as they are immobile. Because they access the larger pores, i.e. grain boundaries, then a disproportionate loss of pores more accessible to the larger N_2 is likely. It appears we have observed a similar effect for desalination of saline recycled wastewater. Although gas permeation is able to provide information of the membrane intactness, direct measurement of the pore morphology of the membrane film would give a better understanding of the pore size. Techniques such as evaporporometry and nano-permporometry [58] may be investigated to further explore membrane pore size. However our application of single gas permeation gave us the ability to rapidly assess the membrane film intactness.

4. Conclusions

An approach to desalinate saline recycled wastewater using a zeolite membrane is proposed, which has the potential to avoid the costly pre-treatment systems needed for current polymer RO membranes. The MFI-type zeolite membrane was made on a tubular α-Al_2O_3 support by the seeded secondary hydrothermal growth method. The membrane was installed into a high pressure test system and feed with saline recycled wastewater sourced from a local treatment plant in Melbourne, Australia. The membrane achieved good reductions for both EC (>70%) and organic compounds (>90%) at an applied pressure of $\geq$ 3 MPa and room temperature (21 ºC). The membrane also showed a high rejection (~90% or above) for Ca^{2+} and Mg^{2+}, and a good rejection (>70%) for K^+ and Na^+. This indicates that the prepared MFI-type zeolite membrane is capable of removing salt to the required levels for salt sensitive reuse applications (i.e. agricultural irrigation). The HPSEC results confirmed that the zeolite membrane has removed the majority of organic compounds from the feed water, some aromatic compounds (molecular weights up to 1000 Daltons) and protein-like substances (molecular weights ~4000–5000 Daltons), however, still remained in the permeate possibly due to diffusion in the defects of the membrane between grain boundaries. Also, the membrane withstood 168,000 ppm.h of chlorine exposure demonstrating its high chemical tolerance enabling simplified cleaning and biofouling control techniques. SEM and gas permeation measurements confirmed the formation of MFI-type silicalite membrane film on the surface of α-Al_2O_3 support, and showed that the membrane remained intact after exposure to the saline recycled wastewater. While the membrane produced reduced organic and salinity water suitable for reuse, further work is needed to improve flux to be comparable to current generation polymer RO membranes.

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Research highlights:

- An approach to desalinate saline recycled wastewater by a MFI-type zeolite membrane is proposed.
- The membrane achieved a rejection of ≥ 90% for Ca^{2+} and Mg^{2+}, and >70% for K^+ and Na^+ at ≥ 3 MPa and 21 ºC.
- The membrane also removed >90% of organic compounds (aromatic and protein-like substances).
- The membrane withstood 168,000 ppmh of chlorine exposure confirming its high chemical tolerance.
- No changes in membrane structure were observed after exposure to the saline recycled wastewater.

Graphical abstract