

# Diffusion behaviour of multivalent ions at low pH through a MFI-type zeolite membrane

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## ABSTRACT

Zeolite membranes have been widely examined for desalination. Work to date has shown effective performance in monovalent rich solutions, but the understanding of the unique ion-zeolite interactions for multivalent ion rich solutions, such as those found in acidic mining wastewaters, has not yet been studied. Filtration performance of MFI-type zeolite membrane was evaluated on a model multivalent ion, Fe<sup>3+</sup>, Al<sup>3+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>, solution with total dissolved solids (TDS) of 97,000 mg L<sup>-1</sup> and pH 2.03 at between 3 MPa and 7 MPa and 21 °C to 70 °C. At 7 MPa and 21°C, rejection for Fe<sup>3+</sup> was 97%, 80% for Al<sup>3+</sup> and Mg<sup>2+</sup>, and 50% for Ca<sup>2+</sup>. This behaviour followed the rejection of ions with larger hydrated diameter, except for Al<sup>3+</sup> which was attributed to its unique strong interaction with zeolites. However, an unusual trend of increasing rejection with increasing temperature was observed. Instead of activated transport which occurs with monovalent or dilute solutions, temperature accelerated the infiltration of multivalent ions into the zeolite structure to further block ions and synergistically increased rejection. Zeolite membranes exhibited unique effects in multivalent ion rich solution

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that could be further utilised in niche desalination applications or benefit other applications such as sensors.

*Keywords:* Zeolite membrane; MFI-type; Ion diffusion; Multivalent ions; Filtration.

## 1. Introduction

Ceramic membranes made from zeolites are good candidates for desalination as they possess the required small pore properties to reject ions while diffusing water [1, 2]. Zeolite membranes, especially MFI-type, have been widely examined for desalination [2-11], and may offer an alternative option for desalination of acidic, metal- and sulphate containing mining wastewaters, where they may have extended service life and increased cleaning ability compared to current polymer membrane technology. The MFI-type zeolite has orthorhombic crystal symmetry with nearly cylindrical, 10-member ring channels. The aperture size of the MFI-type zeolite is around 0.56 nm [4, 12-14], which is smaller than the sizes of hydrated ions (e.g.  $\text{Ca}^{2+}$  0.824 nm,  $\text{Mg}^{2+}$  0.856 nm,  $\text{Fe}^{3+}$  0.914 nm,  $\text{Al}^{3+}$  0.950 nm, [15]) but larger than the kinetic diameter of water (0.276 nm, [15]).

MFI-type zeolite membranes have demonstrated high ion rejections, even for the smallest ions (e.g.  $\text{Na}^+$ ) when working as a reverse osmosis (RO) membrane [8, 10], and also showed great ability to separate dissolved organics from aqueous solution [10, 16]. Our recent work [11] also demonstrated the possibility of avoiding the pre-treatment needed for polymeric RO membranes by using MFI-type zeolite membranes for desalination of saline recycled wastewater. The zeolite membrane also showed no deterioration after extreme chlorine or acid cleaning, enabling simplified cleaning and biofouling control techniques.

The performance of MFI-type zeolite membranes, however, was found not always constant. For example, high rejection (>93%) was achieved for  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$  from 0.3wt% seawater solution [8], and  $\text{Na}^+$  rejection of 99.4% was reported for 0.1 M NaCl solution [10]. Recent work carried out by Garofalo and co-workers also demonstrated high rejections of  $\text{Na}^+$  (99.8% and 99.6% for 0.2 M and 0.9 M NaCl feed solutions, respectively) on scaled-up MFI-type zeolite membranes (30 cm long) by vacuum membrane distillation [17]. However, low ion rejection (e.g. 30% for  $\text{Na}^+$ ) was also observed in our previous study [18]. Although significant fluxes ( $13.8 \text{ L m}^{-2} \text{ h}^{-1}$  and  $8.2 \text{ L m}^{-2} \text{ h}^{-1}$  for 0.2 M and 0.9 M NaCl feed solutions,

respectively) have been achieved on MFI-type zeolite membranes by vacuum membrane distillation [17], fluxes (e.g.  $0.5 - 1.4 \text{ L m}^{-2} \text{ h}^{-1}$  at a pressure of 2.76 MPa [19]) of MFI-type zeolite membranes when working as a RO membrane are lower than polymer RO membranes possibly due to their greater active layer thickness. Membrane water transport resistance is proportional to the dense surface layer thickness and hydrophilic properties. Zeolite membranes ( $3 - 10 \text{ }\mu\text{m}$ ) [2, 3, 11] are much thicker than commercial RO membranes ( $0.2 \text{ }\mu\text{m}$ ) [20, 21]. For MFI-type zeolite membranes to be used commercially, further study is needed to understand the cause of the inconsistent ion rejections and fluxes need to be significantly increased.

Apart from inconsistent ion rejections and low flux of MFI-type zeolite membranes, recent studies also showed that MFI-type zeolites exhibited dynamic behaviour associated with ion interactions in different ion complexes (e.g. seawater, or multivalent ion solution) [18, 22-24]. For example, monovalent cations (e.g.  $\text{K}^+$ ,  $\text{Na}^+$ ) can enter the zeolite lattices, while divalent cations (e.g.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) can be absorbed into the grain boundaries of zeolites [22, 23]. The strong uptake of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  from a multivalent ion solution containing  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  into MFI-type zeolite powders resulted in changes to crystal structure and the porous properties [18]. These changes in structure and porosity could impact on diffusion properties of ions in this material when used as a membrane [18, 22, 23]. Temperature was also found to have an impact on membrane performance. Increasing the testing temperature resulted in an increase in permeate flux, but a decrease in ion rejection [7, 8]. Despite ion diffusion through MFI-type zeolite membranes following the hydrated size of ions, more work is needed to correlate ion diffusion with their size and potentially other factors, such as dynamic ion interactions in different ion complexes and operating temperature. In exploring the unique behaviour of ions within MFI zeolite, we recently reported on the beneficial function of multivalent ions to block defects [18]. However no work has been conducted to date exploring the behaviour of these ions in continuous filtration, in particular, with mining wastewaters which contain solutions rich in multivalent ions. Considering the strong interaction with multivalent ions with MFI-type zeolites to block defects and improve salt rejection of NaCl-rich solutions, it remains unknown how these ions would influence membrane performance benefiting these more specialist applications, or even wider applications involving zeolites exposed to multivalent ion rich solutions such as sensors.

In this study, we deposited MFI-type zeolite seeds on the outer surface of a tubular  $\alpha$ -alumina substrate using the rubbing method [7, 11, 25, 26], and then used the secondary hydrothermal growth to prepare the MFI-type zeolite membrane [7, 11]. The prepared membrane underwent filtration performance testing on a model multivalent ion solution containing  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  with TDS of 97,000 mg L<sup>-1</sup> and pH 2.03. The effects of applied pressure, role of operating temperature and influence of acid cleaning on membrane performance were investigated. The dependence of osmotic pressure on the impact of ion diffusion is discussed. Scanning electron microscopy (SEM) was also used to develop a better understanding of the effect of multivalent ion solution exposure on membrane structure and surface morphology.

## 2. Experimental and methods

### 2.1 Preparation of MFI-type membrane

The MFI-type membrane was prepared by the seeded secondary growth method [7, 11], which involved depositing MFI-type zeolite seeds on the outer surface of a  $\alpha$ - $\text{Al}_2\text{O}_3$  support using a rubbing method [25, 26] followed by growth of the membrane under hydrothermal conditions. This seeded secondary growth method has recently attracted attention as it decouples the nucleation and growth from seed growth, whilst also reducing the demand for the costly structure directing agents [6, 27, 28]. The porous  $\alpha$ - $\text{Al}_2\text{O}_3$  tubular support (95.7%  $\text{Al}_2\text{O}_3$ , apparent porosity 34.9%, external diameter 15 mm, internal diameter 10 mm, length 25 mm, mean pore size  $\sim$ 12.2  $\mu\text{m}$ ) used in this study was supplied by Chosun Refractories Co. Ltd, Korea. The MFI-type zeolite seeds (ZSM-5,  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 360$ ) were purchased from ACS Material, USA. The particle size distribution of the MFI-type zeolite seeds was measured to be between 1,000 nm and 3,000 nm (peaking at  $\sim$ 1,800 nm) by Zetasizer (Malvern Instruments-nano-series) [7]. The secondary growth was conducted by placing the seeded support into a Teflon lined stainless steel autoclave and adding the desired growth solution of 2 mL of 1M tetra-propyl ammonium hydroxide (TPAOH) (Aldrich), 2 mL of tetraethyl orthosilicate (TEOS) (98%, Aldrich) and 36 mL deionised water (DI water). Secondary growth was carried out at 180 °C for 16 hours. After growth, the membrane tube was washed in DI water to remove loose precipitate and was then calcined at 500 °C for 4 h.

## 2.2 Filtration test

Filtration performance of the prepared MFI-type zeolite membrane was analysed for the ion complex model of mining wastewater, using a high pressure test system used in our previous work [7]. The membrane was installed into the stainless steel membrane housing, and model multivalent ion solution was fed at a flow rate of  $5 \text{ mL min}^{-1}$  by a high pressure piston pump (Series 1, LabAlliance, USA) with an applied gauge pressure of up to 7 MPa. The ion complex used in this study was prepared by adding 138 g  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  (AJAX Chemicals, Australia), 205 g  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  (Merck, Australia), 58 g  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  (AJAX Chemicals, Australia) and 1.7 g  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  (Merck, Australia) into 2 L DI water. The solution was filtered by a  $0.45 \mu\text{m}$  membrane filter to remove undissolved solids prior to filtration test. The ion concentrations of the pre-filtered solution were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) (Shimadzu ICPE-9000) and are shown in Table 1.  $\text{Cl}^-$  was not measured as it is assumed to be minor (estimated to be  $\sim 400 \text{ mg L}^{-1}$  based on the amount of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  added) in comparison to other ions (e.g.  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$ ) present in the multivalent ion solution. The pH of the pre-filtered multivalent ion solution was measured to be 2.03.

Table 1 ICP-OES measured ion concentrations present in the pre-filtered multivalent ion feed solution.

<b>Ion</b>	<b>Concentration (<math>\text{mg L}^{-1}</math>)</b>
<b><math>\text{Al}^{3+}</math></b>	5,200
<b><math>\text{Fe}^{3+}</math></b>	4,900
<b><math>\text{Ca}^{2+}</math></b>	140
<b><math>\text{Mg}^{2+}</math></b>	9,000
<b><math>\text{SO}_4^{2-}</math></b>	78,000
<b>Total</b>	97,240

The filtration experiments were conducted in a cross-flow setup (cross flow velocity  $0.1 \text{ cm s}^{-1}$ ) with the feed solution being fed under pressure on the outside and permeating to the inside of the membrane. Although the cross-flow velocity used in this study was small, our experience in testing zeolite membranes at this scale and operating at higher

cross flows has little effect on flux and rejection, as concentration polarisation is not significant at the currently low fluxes of zeolite membranes. Filtration performance of the prepared zeolite membrane was determined by the electrical conductivity (EC) (measured with a portable conductivity meter, Sension 156, HACH) and ICP-OES measured ion concentrations of the multivalent ion feed solution and collected permeate samples. The water samples were diluted prior to measurements. Rejections of EC ( $r_{EC}$ ) and ion  $j$  ( $r_j$ ) were calculated by equation (1) and (2), respectively:

$$r_{EC}(\%) = \frac{(EC_f - EC_p)}{EC_f} \times 100 \quad (1)$$

$$r_j(\%) = \frac{(c_{j,f} - c_{j,p})}{c_{j,f}} \times 100 \quad (2)$$

where  $EC_f$  and  $EC_p$  are measured electrical conductivity for the feed and permeate samples, respectively.  $C_{j,f}$  and  $C_{j,p}$  are ICP-OES measured concentrations of ion  $j$  ( $j = \text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) in the feed and permeate solutions, respectively. Flux ( $J$ ,  $\text{L m}^{-2} \text{h}^{-1}$ ) was calculated according to:

$$J = \frac{v}{At} \quad (3)$$

where  $v$  (L) is the volume of the collected permeate over a given time period,  $t$  (h), and  $A$  the membrane's area ( $\text{m}^2$ ).

The osmotic pressures, effective pressures (driving pressure after overcoming the osmotic pressure) and specific flux for filtration of the multivalent ion feed solution (TDS  $\sim 97,000 \text{ mg L}^{-1}$ ) can be determined using known equations [7, 8, 29]:

$$\pi = iMRT \quad (4)$$

$$P_{\text{effective}} = P_{\text{total}} - (\pi_{\text{feed}} - \pi_{\text{permeate}}) \quad (5)$$

$$J_s = \frac{J}{P_{effective}} \quad (6)$$

where  $\pi$  is the osmotic pressure (MPa),  $i$  is the van't Hoff factor of the solute,  $M$  is the molarity of the salt in solution,  $R$  is the universal gas constant ( $0.008315 \text{ L MPa mol}^{-1} \text{ K}^{-1}$ ) and  $T$  is the system temperature (K),  $p_{effective}$  is the effective pressure (MPa),  $p_{total}$  is the applied gauge pressure when operating under ambient permeate pressures,  $\pi_{feed}$  and  $\pi_{permeate}$  are the osmotic pressure (MPa) estimated from equation (4) for the feed solution and permeate, respectively,  $J_s$  is the specific flux ( $\text{L m}^{-2} \text{ h}^{-1} \text{ MPa}^{-1}$ ), and  $J$  is the flux ( $\text{L m}^{-2} \text{ h}^{-1}$ ) calculated from equation (3). The van't Hoff factor ( $i$ ) expresses how many ions and particles are formed (on an average) in a solution from one formula unit of solute. The van't Hoff factor approaches a whole number (2, 3, and so on) only for very dilute solutions. For example, the ideal numbers of the van't Hoff factor are 5 for both  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{Fe}_2(\text{SO}_4)_3$ , 3 for  $\text{CaCl}_2$  and 2 for  $\text{MgSO}_4$ . However, actual values of the van't Hoff factors are generally less than the predicted number of ions due to the ion pairing effect. The multivalent ion solution used in this study is a mixture of  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{Fe}_2(\text{SO}_4)_3$ ,  $\text{CaCl}_2$  and  $\text{MgSO}_4$ , which makes calculation of a van't Hoff factor more complicated. Based on previous work reported by others (e.g. van't Hoff factor values of 4.4 for  $\text{Fe}_2(\text{SO}_4)_3$  and 1.21 for  $\text{MgSO}_4$  were used to calculate boiling point elevation of a solution containing  $\text{Fe}_2(\text{SO}_4)_3$ ,  $\text{NaCl}$  and  $\text{MgSO}_4$  [30]; van't Hoff factor values of  $\sim 2.6$  for  $\text{CaCl}_2$  and  $\sim 1.2$  for  $\text{MgSO}_4$  were used to determine surface vapour pressure of droplets at various solution concentrations [31]), the present study used the van't Hoff factor values of 4.4 for both  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{Al}_2(\text{SO}_4)_3$ , and 2.6 and 1.2 respectively for  $\text{CaCl}_2$  and  $\text{MgSO}_4$ .

Acid cleaning was used in this study to restore the membrane performance each time the flux dropped significantly due to the blockage of membrane pores during testing with multivalent ion solution. Membrane cleaning was conducted in the same high pressure testing setup. The blocked membrane was flushed with DI water and then fed with 1 M HCl solution on the outside and permeating to the inside at an applied pressure of 7 MPa and  $21^\circ\text{C}$  for 1.5 h followed by DI water flushing under the same conditions for another 1.5 h.

### 2.3 SEM

SEM was employed to investigate any changes in the morphology of the zeolite membrane after filtration testing with multivalent ion solution. Prior to characterisation, the filtration tested membrane underwent acid cleaning and DI water permeation to remove weakly adsorbed material (including ions). The 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.

## 3. Results and discussion

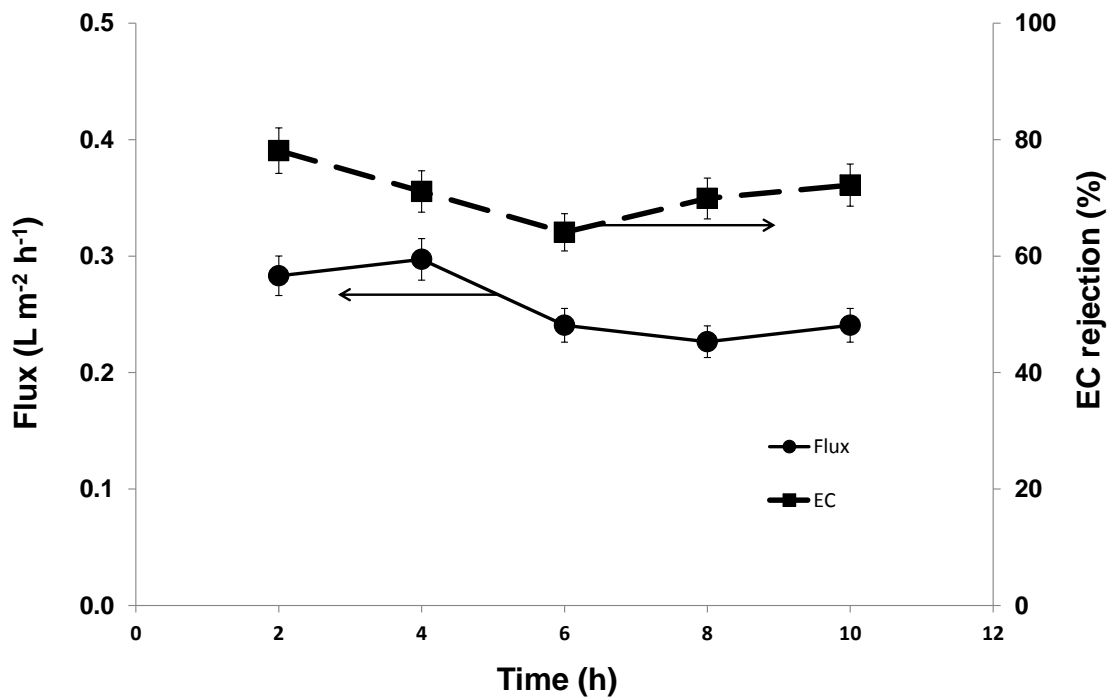
### 3.1. Filtration performance for ions with different hydrated sizes

Prior to filtration of the multivalent ion solution, salt rejection performance of the prepared MFI-type zeolite membrane was evaluated by a NaCl solution (3,000 mg L<sup>-1</sup> TDS). The membrane was initially tested with DI water at an applied pressure of 7 MPa and room temperature (21°C) and the membrane showed a constant flux of 5.6 L m<sup>-2</sup> h<sup>-1</sup>. Following the initial DI water testing, the membrane was tested with NaCl solution (3,000 mg L<sup>-1</sup> TDS) under the same conditions. The membrane showed an average salt rejection of 31% with a flux of 2 L m<sup>-2</sup> h<sup>-1</sup> at an applied pressure of 7 MPa and room temperature (21°C). This is lower than that expected for zeolite desalination membranes, where >90% salt rejections are expected [8, 10], but shows an intact zeolite coating with some non-selective water flux through defects. This membrane may be suitable for NF applications to reject larger cations and anions.

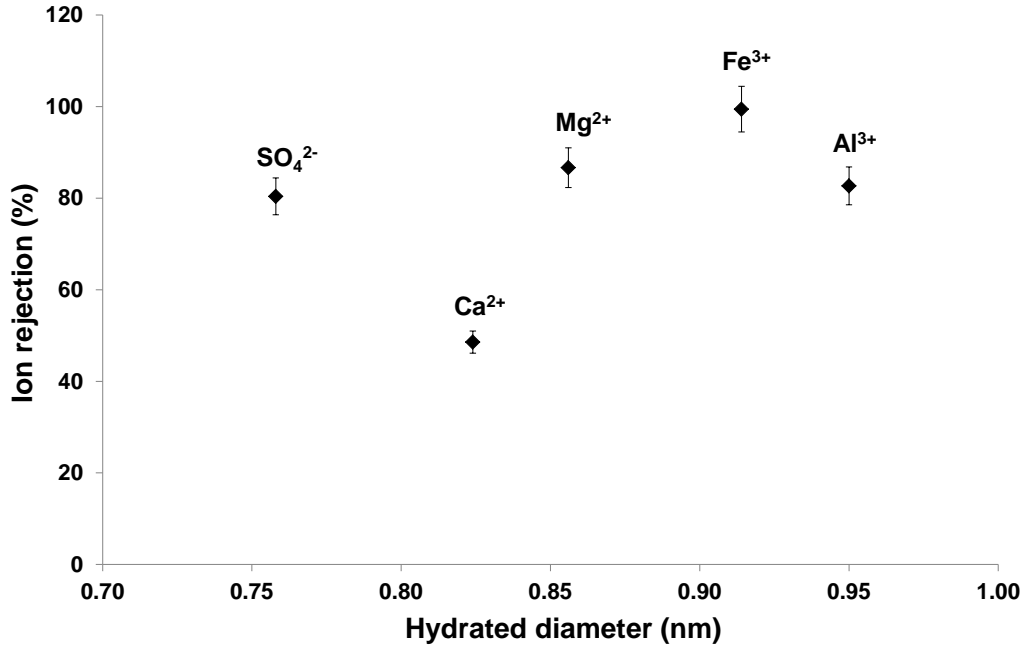
After testing with NaCl solution, the membrane was flushed with DI water and filtration of the multivalent ion solution (TDS ~97,000 mg L<sup>-1</sup>; Table 1) was then carried out under the same conditions (7 MPa and 21°C). ICP-OES was used to measure the concentrations of the major ions present in the feed (multivalent ion solution) and permeate samples obtained from the filtration testing. Figure 1 shows the EC rejection and water flux achieved on the prepared MFI-type zeolite membrane for the multivalent ion solution. The ion rejections calculated from the ICP-OES results are shown in Figure 2. Both flux and rejection over the 8 hour test period varied slightly. The membrane achieved an EC rejection of 71 % and water flux of ~0.25 L m<sup>-2</sup> h<sup>-1</sup> at an applied pressure of 7 MPa (Fig. 1). The ICP-OES results showed a high rejection for all the major ions (99 % for Fe<sup>3+</sup>, 83 % for Al<sup>3+</sup>, 87 % for Mg<sup>2+</sup> and 80 % for SO<sub>4</sub><sup>2-</sup>) present in



the synthetic mining water except for  $\text{Ca}^{2+}$  (48 %) (Fig. 2). These rejections are higher than that obtained above for the NaCl solution (3,000 mg L<sup>-1</sup> TDS) (31%) at the same operating conditions. This is expected as these ions ( $\text{Ca}^{2+}$  0.824 nm,  $\text{Mg}^{2+}$  0.856 nm,  $\text{Fe}^{3+}$  0.914 nm,  $\text{Al}^{3+}$  0.950 nm, [15]) present in the ion complex are all larger than  $\text{Na}^+$  (0.716 nm, [15]) in hydrated form. Interestingly it was also found that the largest ion  $\text{Al}^{3+}$  did not show the highest rejection, while the smallest ion  $\text{SO}_4^{2-}$  showed a relatively high rejection (Fig. 2). This interesting finding will be discussed later. For  $\text{Ca}^{2+}$ , it should be pointed out that its concentration (140 mg L<sup>-1</sup>) is significantly lower than other cations (~5000 mg L<sup>-1</sup> or above) in the feed (Table 1), and the water samples were diluted prior to measurements (Section 2.2). For the cations having concentration of (~5000 mg L<sup>-1</sup> or above) to be measured by ICP-OES, a larger dilution factor (e.g. 1:50 to 1:100) is needed compared to that required for  $\text{Ca}^{2+}$ . This large dilution factor resulted in greater errors (5 – 10%) to the calculation of rejection for  $\text{Ca}^{2+}$  compared to the error for the metals in higher concentration based on the measurement uncertainty of ICP-OES at low concentrations.



**Fig. 1 EC rejection and water flux on the prepared MFI-type zeolite membrane with the pre-filtered multivalent ion solution (Table 1) fed at 7 MPa at 21 °C.**



**Fig. 2 Rejection of ions with different hydrated sizes on the prepared MFI-type zeolite membrane fed with multivalent ion solution at an applied pressure of 7 MPa and 21 °C.**

It is well known that the MFI-type zeolite has an effective intra-crystal pore diameter of approximately 0.56 nm [3, 4, 14], which is smaller than the size of hydrated  $\text{Na}^+$  (0.716 nm) [15]. A molecular dynamics simulation study showed that complete rejection of hydrated  $\text{Na}^+$  may be achieved on a perfect membrane without inter-crystalline pores [1]. However, another molecular dynamics simulation study on MFI-type zeolites identified that multivalent cations cannot enter the intrinsic zeolite pores, while monovalent cations such as  $\text{K}^+$  and  $\text{Na}^+$  can but are hindered by the inability of the counter ion ( $\text{Cl}^-$ ) to enter yielding a desalination effect via the need for charge neutrality [32]. Hence, desalination by size exclusion can occur for transport through the intrinsic zeolite pores.

However, for the larger inter-crystalline pores that are also present on an actual membrane, transport of both hydrated cations and anions can occur [3]. Considering the sizes of the cations in the present case, it is noted that  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  have sizes of 0.950 nm, 0.914 nm, 0.824 nm and 0.856 nm, respectively [15]. None of these ions would physically fit into the MFI pores (0.56 nm) as they are all approximately double the pore size and rejection of divalent ions present in seawater by the crystal was confirmed in previous work [8, 23]. However, the contribution of the inter-crystalline spaces probed with positron annihilation lifetime

spectroscopy has been explored previously and revealed that small grain boundaries are around 1 nm in diameter [22, 23]. At this size the inter-crystalline spaces allow the entrance of these < 1 nm ions. However in solutions containing electrolytes, zeolite surface charge plays an important role in individual ion diffusion. Noack and co-workers explored the surface charge of zeolite powders down to pH 3 [33], an effect which will govern the selectivity of diffusing ions in solution because the electrostatic potential has an effect to change the effective pore size conditional to the charge of the ion. Since alumina can be incorporated into the zeolite framework during membrane preparation due to the dissolution of the Al<sub>2</sub>O<sub>3</sub> surface in the high NaOH concentration synthesis solution and solid-state diffusion of Al<sup>3+</sup> during calcinations [34], Al<sub>2</sub>O<sub>3</sub>-supported MFI membranes are generally not Al free in their frameworks despite the use of Al-free synthesis solutions [3, 35]. At low pH, alumina containing zeolites exhibited a weaker negative charge which would suggest anions would be more weakly repelled. SO<sub>4</sub><sup>2-</sup> was the most dominant anion (0.758 nm, [15]) in this system, and at pH 2 conditions may be more favourably permeated as the counterion than Cl<sup>-</sup> to any permeated cation. This anion appeared with the smaller hydrated size of Ca<sup>2+</sup> which also showed the lowest rejection in the system (Fig. 2). The highest rejection was observed for Fe<sup>3+</sup> and correlated with its relatively larger hydrated size (Fig. 2). However, the largest ion, Al<sup>3+</sup>, exhibited a smaller rejection than Fe<sup>3+</sup> and Mg<sup>2+</sup> (Fig. 2). Li et al. [3] investigated RO separation of ions from aqueous solutions and found that complete rejection is possible for hydrated Al<sup>3+</sup> by size exclusion on a MFI-type membrane, but not for the other hydrated ions including Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>. In their study, the tests were conducted at pH 7 where the membrane would be strongly negatively charged leading to the highest rejections for Al<sup>3+</sup>. For this work modelled from a mining water solution with pH closer to 2 (leading to a slightly positively charged membrane) a low rejection of Al<sup>3+</sup> was obtained when compared to Fe<sup>3+</sup> and Mg<sup>2+</sup> (Fig. 2). It would seem size exclusion of the largest ion is consistent with Li's results [3], but in this case the larger Al<sup>3+</sup> was favoured to diffuse relative to Fe<sup>3+</sup> in the membrane. Lower rejection of Al<sup>3+</sup> in comparison with Fe<sup>3+</sup> on zeolite membranes has also been reported by other researchers [36-38]. Basumatary [36] used FAU zeolite membrane to separate Al<sup>3+</sup> and Fe<sup>3+</sup> from an aqueous solution with pH of 2, and found that Al<sup>3+</sup> (e.g. 75%) had a lower rejection than Fe<sup>3+</sup> (e.g. 81%). FAU zeolite has pores formed by a 12-membered ring with a diameter of 0.74 nm, which is larger than that of MFI zeolites but smaller than the sizes of hydrated ions (e.g. Fe<sup>3+</sup> 0.914 nm, Al<sup>3+</sup> 0.950 nm, [15]). Shukla and co-workers [37] studied analcime zeolite–clay composite membranes for separation of chloride salts of trivalent cations (FeCl<sub>3</sub> and AlCl<sub>3</sub>). Analcime zeolite has irregular channels formed by highly distorted 8-rings with pore diameter of 0.42×0.16 nm. Their study also

observed a lower rejection of  $\text{AlCl}_3$  (e.g. 90%) when compared to  $\text{FeCl}_3$  (e.g. 96%). They suggested that this may be due to accumulation of  $\text{AlCl}_3$  in the boundary layer on the upstream side of the membrane, as the surface concentration increases the permeate concentration is also increased, thus leading to a lower value of the observed rejection for  $\text{AlCl}_3$ . Our previous study on the uptake of multivalent ions  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  into MFI-type zeolite powders [18] found  $\text{Al}^{3+}$  was adsorbed the most by the zeolites amongst the cations present in the solution in terms of their molar quantity normalised to the weight of the zeolites. This supports the higher surface concentration effect of  $\text{Al}^{3+}$  concluded by Shukla and co-workers [37], where although the materials were different, both still possessed an aluminosilicate chemistry which may lead to a similar mechanism of dissolved alumina attraction to the solid surface. We also observed from the same study [18] that the binding strength of ions adsorbed by the zeolites were different, and  $\text{Al}^{3+}$  and  $\text{Ca}^{2+}$  appeared to be relatively more easily washed out by HCl cleaning or DI water flushing when compared to  $\text{Fe}^{3+}$  and  $\text{Mg}^{2+}$ . Therefore, if a solubility-diffusivity mode of transport through the membrane is considered, it suggests  $\text{Al}^{3+}$  has a larger solubility and diffusion within the zeolite membrane compared to  $\text{Fe}^{3+}$  and  $\text{Mg}^{2+}$  leading to greater permeability.

It was also found that the flux ( $\sim 0.25 \text{ L m}^{-2} \text{ h}^{-1}$ ) achieved for the multivalent ion solution (Fig. 1) was 8-fold lower than that obtained for NaCl solution ( $3,000 \text{ mg L}^{-1}$  TDS) at the same operating conditions ( $2 \text{ L m}^{-2} \text{ h}^{-1}$ ). The lower flux compared to NaCl solution testing can be attributed to the reduced driving force for the relatively higher ionic strength solution, and in turn higher osmotic pressure needed to be overcome in order for RO to occur. Table 2 shows the osmotic pressures of the feed ( $\pi_{\text{feed}}$ ) and permeate ( $\pi_{\text{permeate}}$ ), effective pressure ( $p_{\text{effective}}$ ) and specific flux ( $J_s$ ) determined according to Equations 4 to 6. The feed osmotic pressure,  $\pi_{\text{feed}}$ , of the NaCl solution ( $3,000 \text{ mg L}^{-1}$  TDS) was estimated to be 0.23 MPa. The osmotic pressure for the multivalent ion feed solution ( $97,000 \text{ mg L}^{-1}$  TDS) was calculated to be 2.6 MPa (Table 2). The corresponding effective pressure,  $p_{\text{effective}}$ , was determined to be  $\sim 6.9$  MPa and  $\sim 4.8$  MPa, respectively, at a total applied pressure of 7 MPa and operating temperature of 21 °C. In our previous study [7] on the desalination of NaCl solutions, flux decreased when the concentration of feed NaCl solution was increased from  $3000 \text{ mg L}^{-1}$  to  $90,000 \text{ mg L}^{-1}$  due to the reduction in the effective driving pressure with the increased salinity of feed solutions. However, the specific flux was found almost unchanged when the concentration of the feed NaCl solution was increased. In this work, a significant difference in the specific flux (Table 2) was observed between the two feed solutions tested under the same conditions (7 MPa and 21 °C). The

specific flux calculated for the multivalent ion solution was 5-fold smaller than that for the NaCl solution (Table 2). While the driving force was lower for the multivalent ion solution (~4.8 MPa) compared to the NaCl solution (~6.9 MPa), the specific flux of the multivalent ion solution based on net driving pressure should remain almost unchanged if no other effects are involved [7]. Significant low specific flux observed for the multivalent ion solution in this study indicated that the membrane pores have been blocked during testing with the multivalent ion solution, and is indeed the case where in our previous work a similar solution effectively caused a flux reduction tested on the same NaCl solution (before and after exposure to the multivalent ion solution) due to blocking by the multivalent ions (e.g. Fe<sup>3+</sup> and Al<sup>3+</sup>) [18].

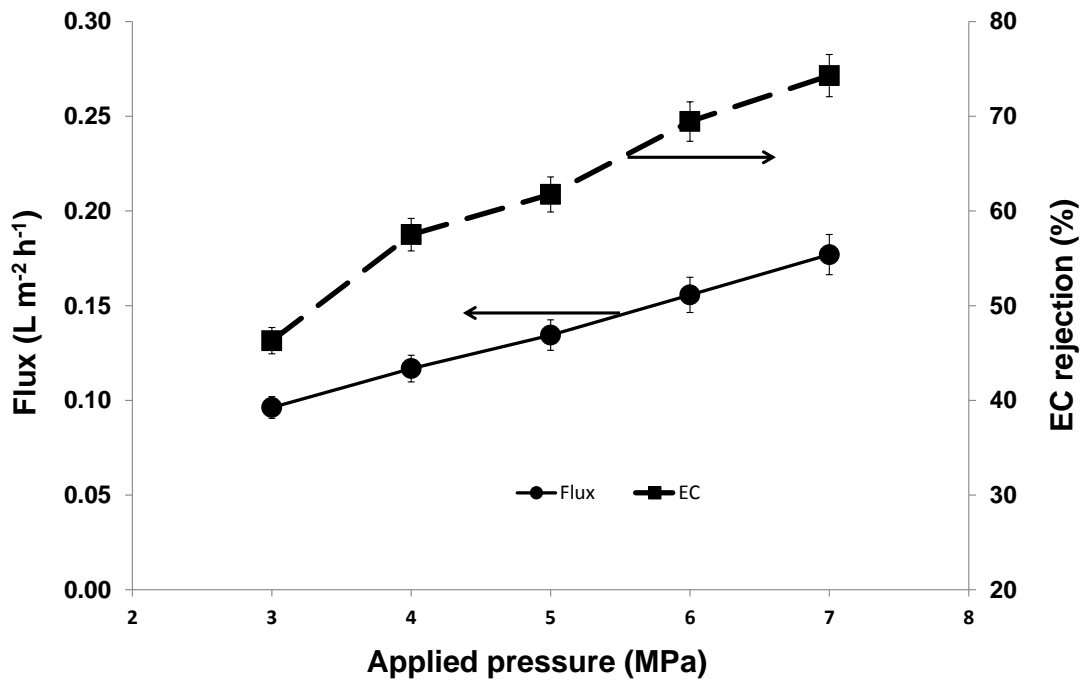
Table 2 Osmotic pressures of feed,  $\pi_{feed}$ , and permeate,  $\pi_{permeate}$ , effective pressure,  $p_{effective}$ , and specific flux,  $J_s$ , determined for the NaCl solution (TDS 3,000 mg L<sup>-1</sup>) and multivalent ion solution (TDS ~97,000 mg L<sup>-1</sup>) used in this study. Values determined for tests performed at 7 MPa and 21 °C.

<b>Feed solution</b>	$\pi_{feed}$ (MPa)	$\pi_{permeate}$ (MPa)	$p_{effective}$ (MPa)	$J_s$ (L m <sup>-2</sup> h <sup>-1</sup> MPa <sup>-1</sup> )
<b>NaCl (TDS 3,000 mg L<sup>-1</sup>)</b>	0.23	0.16	6.9	0.29
<b>Multivalent ion solution (TDS ~97,000 mg L<sup>-1</sup>)</b>	2.6	0.44	4.8	0.052

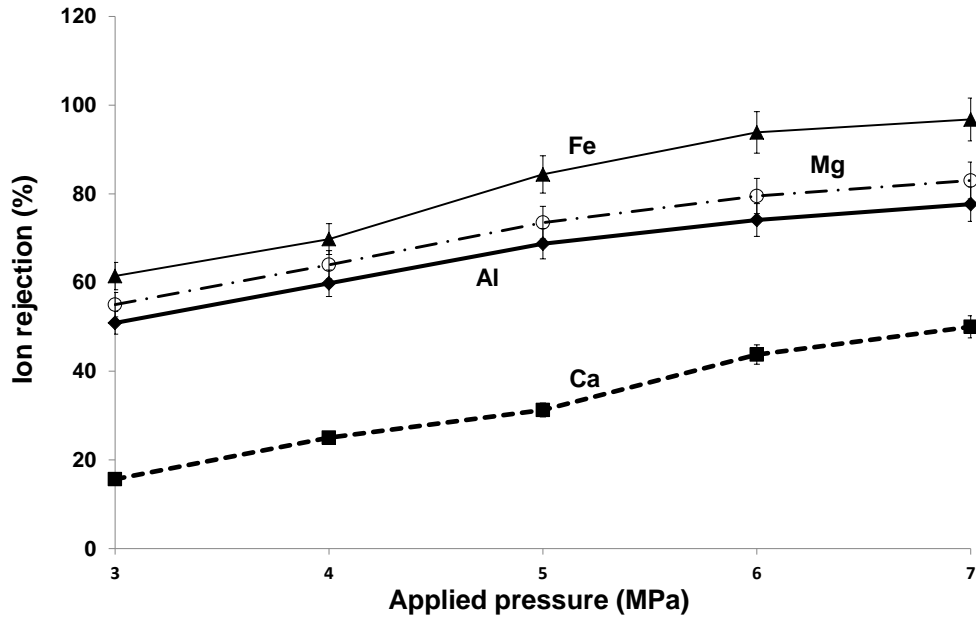
### 3.2. Filtration performance under different applied pressures

The effect of applied pressure on membrane performance for filtration of the multivalent ion solution was investigated at different applied pressures (3 – 7 MPa) and 21 °C. Since the membrane pores were blocked by the ions present in the multivalent ion solution during the initial filtration testing, the membrane was cleaned with acid (1 M HCl solution) and DI water prior to further testing at different applied pressures. No further membrane clean was conducted between each pressure testing. Figures 3 and 4 show the results obtained from the filtration test with the multivalent ion solution at different applied pressures (3 – 7 MPa) and room temperature (21 °C). It can be clearly seen from Figure 3 that both EC rejection and water flux increased with an increase of the applied pressure. The flux increased by > 50% when the applied pressure was increased from 3 MPa to 7 MPa. The ICP-OES results (Fig. 4) confirmed

that higher applied pressure (up to 7 MPa) gave higher ion rejection. As expected the membrane achieved a high rejection for  $\text{Fe}^{3+}$  when the operating pressure was applied at 5 MPa or above (from ~84% at 5 MPa up to ~97% at 7 MPa), a good rejection for  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$  (from ~70% at 5 MPa to ~80% at 7 MPa) but less rejection for  $\text{Ca}^{2+}$  (up to 50%) at the same operating conditions (Fig. 4).



**Fig. 3 EC rejection and water flux achieved on the prepared MFI-type zeolite membrane, fed with multivalent ion solution at different applied pressures (3 – 7 MPa) and 21 °C.**



**Fig. 4 Ion rejections on the prepared MFI-type zeolite membrane fed with multivalent ion solution at different applied pressures (3 – 7 MPa) and 21 °C.**

The results obtained from filtration performance testing under different applied pressures (3 – 7 MPa) appear to follow the effect related to change in net driving pressure after overcoming the osmotic pressure [7]. Similar trends were observed from our previous study on the desalination of saline recycled wastewater, where EC reduction increased from ~56% to ~80% and the flux increased an order of magnitude when the applied pressure was increased from 1 MPa to 7 MPa [11]. The effective pressures (Table 3) calculated based on the ion rejections (Fig. 4) achieved by the membrane confirmed a significant increase in effective pressure when increasing the applied pressure from 3 MPa to 7 MPa. However, there was a slight decrease in specific flux (Table 3) although the flux increased with an increase of the applied pressure (Fig. 3). This indicated that the zeolite membrane pores might have been blocked by infiltration of ions under higher pressure operation. Our earlier work [18, 22, 23] has identified that monovalent cations (e.g.  $K^+$ ,  $Na^+$ ) can enter the zeolite lattices, while divalent cations (e.g.  $Ca^{2+}$ ,  $Mg^{2+}$ ) and trivalent cations (e.g.  $Fe^{3+}$ ,  $Al^{3+}$ ) can occupy the grain boundaries of zeolites upon exposure to ion solutions, and this can result in changes to crystal structure and the porous properties of zeolites. While this effect was observed at ambient pressure, increasing in pressure at least can cause flow through the membrane to ensure penetration of ions into the zeolite film, thus enhancing the blockage of membrane pores. It is also possible that grain boundaries of zeolites are compacting under relative high pressure (e.g. 7 MPa). Although it

has been reported that the zeolites unit cell can expand under extremely high pressures (e.g. at GPa scales) [39, 40], to our knowledge, no existing research addressed compressibility of the grain boundaries of zeolites under pressures at MPa scales, possibly because it is unmeasurable under such pressure level.

Table 3 Osmotic pressures of feed ( $\pi_{feed}$ ) and permeate ( $\pi_{permeate}$ ), effective pressure ( $p_{effective}$ ), and specific flux ( $J_s$ ) estimated for desalination of the multivalent ion feed solution (TDS  $\sim 97,000 \text{ mg L}^{-1}$ ) under different applied pressures ( $p_{total} = 3 - 7 \text{ MPa}$ ) at  $21 \text{ }^\circ\text{C}$ . Values determined based on the ion rejections (Fig. 4).

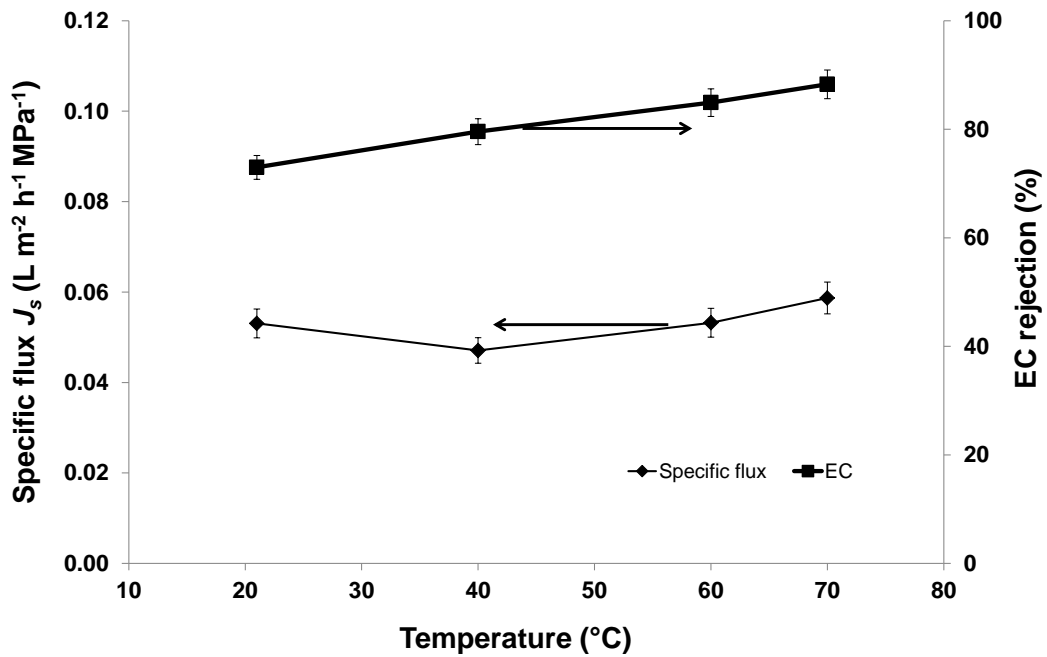
$p_{total}$ (MPa)	$\pi_{feed}$ (MPa)	$\pi_{permeate}$ (MPa)	$p_{effective}$ (MPa)	$J_s$ ( $\text{L m}^{-2} \text{ h}^{-1} \text{ MPa}^{-1}$ )
3	2.6	1.2	1.6	0.060
4	2.6	0.97	2.4	0.049
5	2.6	0.70	3.1	0.043
6	2.6	0.53	3.9	0.040
7	2.6	0.44	4.8	0.037

### 3.3. Effect of temperature on filtration performance

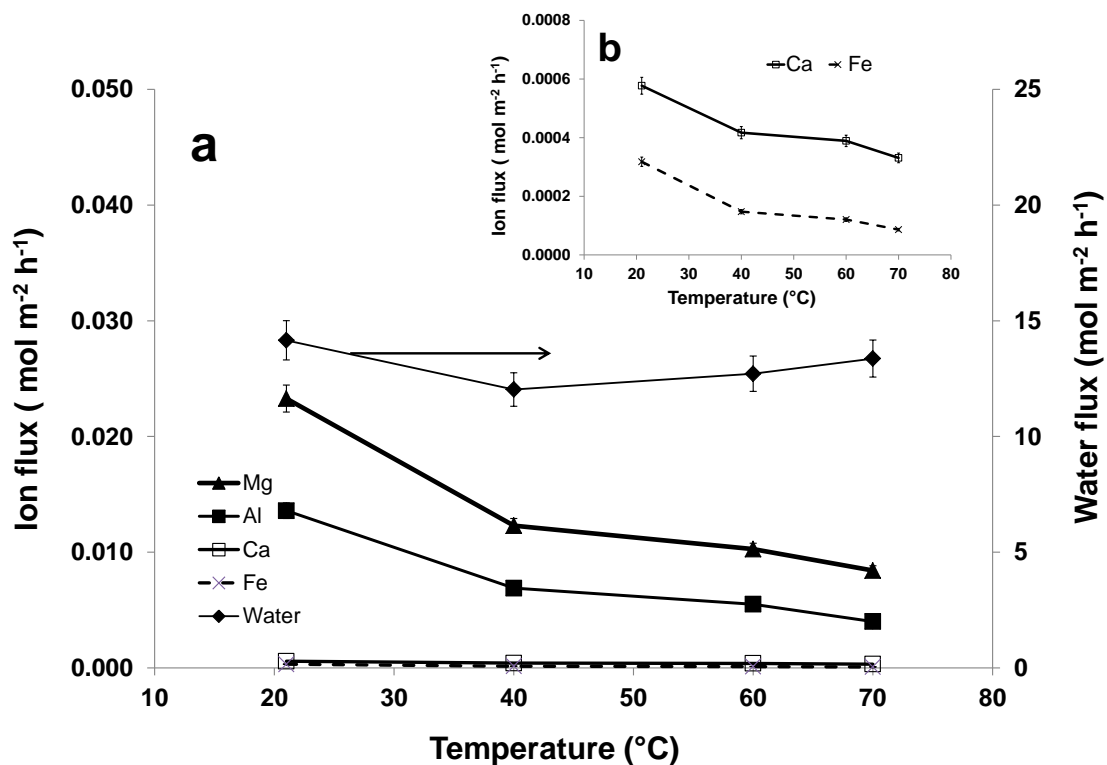
The prepared MFI-type zeolite membrane was also tested for filtration with the multivalent ion solution at an applied pressure of  $7 \text{ MPa}$  and different temperatures up to  $70 \text{ }^\circ\text{C}$  after another acid clean. Figure 5 shows the average EC rejection and specific flux ( $J_s$ ) achieved on the prepared MFI-type zeolite membrane for the multivalent ion solution. The average of water and ion fluxes, and ion rejection for each temperature are shown in Figures 6 and 7, respectively. The values of EC rejection, specific flux, water and ion fluxes, and ion rejection shown in Figures 5 – 7 were averaged from the stabilised values for each temperature. The results obtained from the testing at different temperatures showed that the average EC rejection increased with an increase in test temperature (Fig. 5). However, there was only a slight change in specific flux when increasing the temperature (Fig. 5). The stabilised absolute water flux values were slightly lower than expected when tested at high temperature (e.g.  $0.22 \text{ L m}^{-2} \text{ h}^{-1}$  for  $40 \text{ }^\circ\text{C}$ ,  $0.23 \text{ L m}^{-2} \text{ h}^{-1}$  for  $60 \text{ }^\circ\text{C}$ , and  $0.24 \text{ L m}^{-2} \text{ h}^{-1}$  for  $70 \text{ }^\circ\text{C}$ ) when compared to that at low temperature ( $0.25 \text{ L m}^{-2} \text{ h}^{-1}$  at  $21 \text{ }^\circ\text{C}$ ), and flux decreased for all ions when increasing the



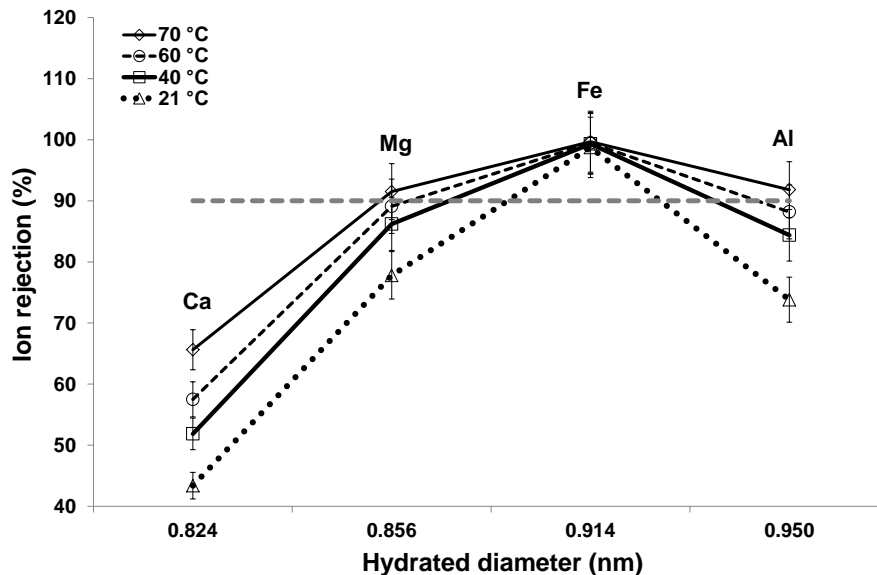
temperature (Fig. 6). The ion rejections confirmed that higher operating temperature (up to 70 °C) gave higher ion rejection, in particular  $\text{Ca}^{2+}$  which has the smallest hydrated diameter but showed a largest increase in rejection (Fig. 7). The membrane achieved a high rejection for  $\text{Fe}^{3+}$  (99%),  $\text{Al}^{3+}$  (92%) and  $\text{Mg}^{2+}$  (91%) but less rejection for  $\text{Ca}^{2+}$  (66%) at an applied pressure of 7 MPa and feed temperature of 70 °C (Fig. 7).



**Fig. 5 EC rejection and specific flux on the prepared MFI-type zeolite membrane, fed with multivalent ion solution at different temperatures under an applied pressure of 7 MPa.**



**Fig. 6** Water and Ion fluxes on the prepared MFI-type zeolite membrane fed with multivalent ion solution at an applied pressure of 7 MPa and different temperatures.



**Fig. 7** Rejection of ions with different hydrated sizes on the prepared MFI-type zeolite membrane fed with multivalent ion solution at an applied pressure of 7 MPa and different temperatures.

It is known that osmotic pressure is also a function of temperature shown in Equation 4 [29], so net driving pressure after overcoming the osmotic pressure (effective pressure) will also depend on the test temperature. When the testing temperature was increased from 21 °C to 70 °C at a total applied pressure ( $p_{total}$ ) of 7 MPa, the feed osmotic pressure,  $\pi_{feed}$ , of the multivalent ion solution (97,000 mg L<sup>-1</sup> TDS) increased from 2.6 MPa to 3.1 MPa, while the corresponding effective pressure,  $p_{effective}$ , decreased from 4.8 MPa to 4.1 MPa (determined according to Equations 4 – 5). Lower effective pressure generally results in lower water flux and ion rejection if no other effects are involved [11]. For the results here, however, it seems that increasing the temperature decreased ion fluxes (Fig. 6) but increased the overall ion rejection (Fig. 7) and had no significant impact on specific flux and the absolute water flux (Figs 5 and 6). Our previous study on desalination performance of a MFI-type zeolite membrane for a NaCl feed solution (TDS 3000 mg L<sup>-1</sup>) under an applied pressure of 7 MPa showed that flux doubled when the testing temperature was increased from 21 °C to 90 °C [7]. Our another study on desalination of sea salts solution also showed that the specific flux increased 2.5-fold when the operating temperature was increased from 22 °C to 90 °C [8]. Increase in permeate flux with increasing temperature is typical for microporous materials, especially MFI-type zeolites as observed in pervaporation studies which is attributed to activated transport [9, 41]. Activated diffusion was also observed by Li et al. [4] in desalination through the same structures. In their study both water and ion fluxes were found to increase significantly when raising the feed temperature from 10 °C to 50 °C. However, the changes in absolute water flux and specific flux in this study were insignificant when compared to that observed in our previous work [7, 8]. The same studies [7, 8] also showed a decrease in the rejection of cations when increasing the testing temperature. Therefore, in our work concerning the higher valency ions, another effect is dominating giving the observed unique behaviour. It is known that increasing temperature could reduce the apparent size of hydrated ions [42] and increase the zeolite intrinsic pores with the upper limit of pore size of around 0.6 nm (approaching the size of the hydrated Na<sup>+</sup> and Cl<sup>-</sup>) as determined by positron annihilation lifetime spectroscopy (PALS) [8]. This means that the hydration diameter decreases at the same time as the zeolite intrinsic pores open, leading to a decrease in ion rejection especially for monovalent ions which have a relatively small hydrated diameter (e.g. Na<sup>+</sup>, K<sup>+</sup>). It was also found from PALS measurements that the microporous grain boundaries decreased in size with increasing temperature [8]. In our case here when increasing temperature, the membrane appeared to have reduced in pore size to substantially reject Mg<sup>2+</sup> (90% rejection close to 0.86 nm) where at ambient temperature it was < 80% rejected (90% rejection close to 0.89 nm, i.e. between hydrated diameter of Mg<sup>2+</sup>

and  $\text{Fe}^{3+}$ ) (Fig. 7). The significant increase in rejection of the smallest ion  $\text{Ca}^{2+}$  (although it did not reach 90%) with increasing in temperature as observed here (Fig. 7) suggested that the small pore tail of the membrane pore size distribution might be also reduced.  $\text{Al}^{3+}$  also showed an increase in rejection when temperature was increased, however, it was not the most rejected ion in the system which was  $\text{Fe}^{3+}$  (Fig. 7). This was unusual because  $\text{Al}^{3+}$  (0.950 nm) is reported to have a larger hydrated diameter compared to  $\text{Fe}^{3+}$  (0.914 nm) [15], however it may be apparently smaller due to its known strong uptake into the zeolite like iron but weaker interaction with zeolite material compared to  $\text{Fe}^{3+}$  [18]. At pH 2, both  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  can strongly adsorbed on the silica surface and have a greater tendency to form covalent bonds than  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  [43], therefore they both can strongly chelate with the silicalite surface [44, 45]. However,  $\text{Al}^{3+}$  might be easy to release due to its relatively weaker interaction than  $\text{Fe}^{3+}$  [18].  $\text{Al}^{3+}$  has slightly stronger hydration energy [46] than  $\text{Fe}^{3+}$  [47] ( $-4665 \text{ kJ mol}^{-1}$  and  $-4430 \text{ kJ mol}^{-1}$  respectively), therefore can retain water molecules more strongly than  $\text{Fe}^{3+}$ . This enables  $\text{Fe}^{3+}$  to preferentially interact with the silicalite network and be retained by the membrane.  $\text{Al}^{3+}$  on the other hand diffuses more freely as it strongly retains water molecules instead of networking with silicalite.

Thermal energy effects on molecule interactions may also explain the lower  $\text{Al}^{3+}$  rejection than expected. Increasing temperature can influence the ion-water interactions and water-water interactions in an ion solution [42]. For example, the water-water interactions can be weakened by increasing temperature, and this will result in an effect where the ions hold the water molecules more tightly and the ion-water distance contracts [48]. However, when temperature was raised,  $\text{Al}^{3+}$  would tightly hold the water molecules and together with the ion-water distance contraction, the apparent size of its hydrated form is reduced. The apparent size of  $\text{Al}^{3+}$  here appeared closer to  $\text{Mg}^{2+}$  in terms of rejection. Al is only one atomic unit larger than Mg, and very similar in terms of atomic weight ( $27 \text{ g mol}^{-1}$  vs  $24 \text{ g mol}^{-1}$ ), and much lighter compared to Fe ( $56 \text{ g mol}^{-1}$ ). The increase in overall ion rejection and insignificant changes in specific flux observed here might be also attributed to the blockage of membrane pores by deep penetration of ions at higher testing temperature. Our previous study [18] found that a strong uptake of multivalent ions (e.g.  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ) into MFI-type zeolites occurred during exposure to a solution containing  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , and the adsorbed ions (e.g.  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ) occupied the larger micropores (grain boundaries). The unique ion blocking effect from the infiltration of multivalent ions, particularly for the irreversibly adsorbed  $\text{Fe}^{3+}$  in the zeolite pores, has demonstrated improvement to performance as salt rejecting (water selective) desalination

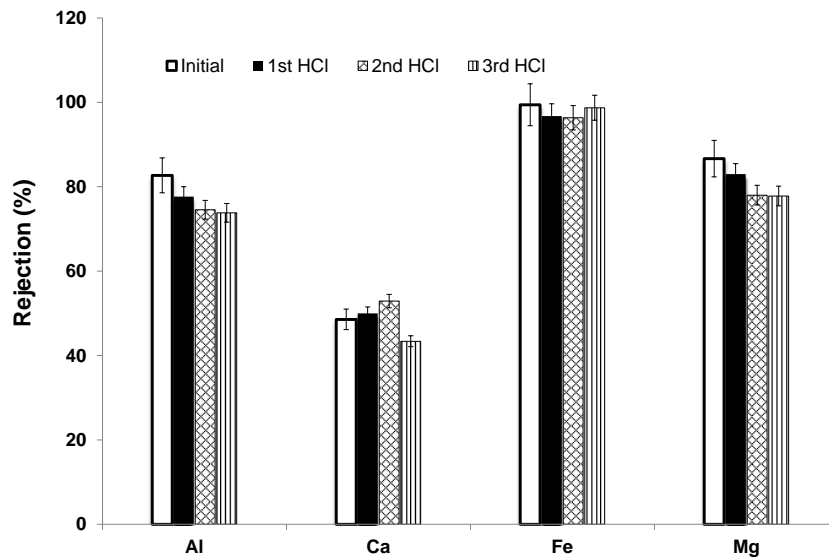
membranes [18]. For the results here, it seems that increasing temperature might accelerate ions to enter the zeolite pores as is expected from activated diffusion observed in the previous studies [4, 9, 41]. The simultaneous decrease in the size of the microporous grain boundaries with increasing temperature as observed by PALS [8] for these ions uniquely very close to their hydrated diameter caused enhanced ion blocking. This translated ultimately to a decrease in ion flux (Fig. 6) and an increase in ion rejection (Fig. 7) even though the effective pressure decreased when increasing temperature.

Water behaviour within zeolites has been well documented by both experiment and simulation [4, 32, 49, 50]. Temperatures can affect the phase condition of water molecules inside the zeolite pores during the mass transfer. For example, in MFI-type silicalite zeolites, water appears to be mostly in form of amorphous solidlike clusters at very low temperatures (< 225 K); at intermediate temperatures (e.g. 225 – 350 K), the behavior of water is almost liquidlike, whereas at higher temperatures, it shows a vaporlike features [49]. Based on the temperatures (294 – 343 K) tested on a MFI-type zeolite membrane in our study, the phase condition of water molecules is almost liquidlike [49].

#### *3.4. Effect of acid clean on filtration performance*

During filtration testing on the multivalent ion feed solution, the membrane pores were blocked several times due to interactions between ions (e.g.  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ) present in the feed solution and the zeolite material [18]. Each time the flux dropped significantly due to the blockage of membrane pores, the membrane was cleaned using 1 M HCl and was then retested for filtration of the multivalent ion solution. Figure 8 compares the ion rejections achieved by the zeolite membrane from the initial test and after several HCl cleans of the multivalent ion solution tested membrane at an applied pressure of 7 MPa and 21 °C. It can be seen from Figure 8 that the ion rejection for  $\text{Fe}^{3+}$  achieved by the membrane after the third HCl clean showed a similar level of removal to those obtained from the initial filtration testing and after the previous two HCl cleans on the same multivalent ion solution under the same operating conditions. A slight decrease in rejections for the other ions was observed after the third HCl clean when compared to the results obtained from the initial filtration testing.  $\text{Ca}^{2+}$  showed a slight higher rejection after the second acidic cleaning when compared to the initial results. This might be due to the measurement errors caused by the larger dilution factor (e.g. 1:50 to 1:100) as mentioned earlier in Section 3.1. However, the change in the rejection of  $\text{Ca}^{2+}$  was within the

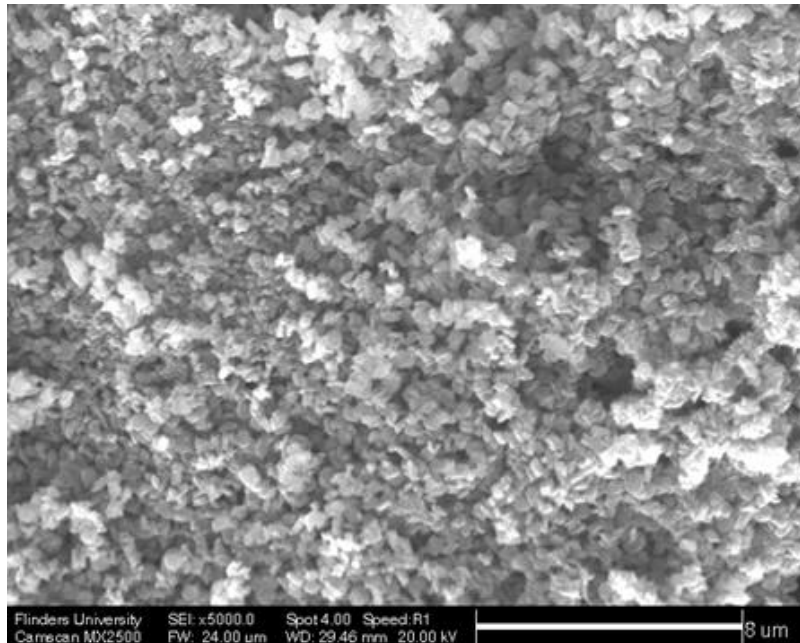
error range of 5 – 10% (Section 3.1). These results indicate that acid (1 M HCl) cleaning of the multivalent ion solution tested membrane did not have a significant impact on the membrane's ion rejection ability. However, the DI water fluxes at an applied pressure of 7 MPa and 21 °C after the acid (1 M HCl) cleans (ranged from 1.0 to 1.4 L m<sup>-2</sup> h<sup>-1</sup>) were significantly smaller than the initial DI water flux (5.6 L m<sup>-2</sup> h<sup>-1</sup>), indicating that the water flux was not fully recovered after 1 M HCl cleaning due to the tight binding of the cations (in particular Fe<sup>3+</sup>) in the zeolite material [18]. Our previous study on membrane performance on saline recycled wastewater showed that the MFI-type zeolite membrane can withstand strong chlorine exposure (168,000 ppm h) demonstrating its high chemical tolerance [11]. High chemical stability of MFI-type zeolite membranes was also demonstrated in other applications such as gas separation [51] and pervaporation [52]. The results obtained here provide evidence of the strong chemical stability of MFI-type zeolite and its suitability for robust NF membrane applications. While here we reported the preliminary work of using acid to clean ion-blocked membrane and to check membrane's chemical stability, optimising the cleaning procedure is necessary for future work when applied for treatment of real mining wastewater.



**Fig. 8 Comparison of ion rejections achieved by the zeolite membrane from the initial test and after 1 M HCl cleans following filtration of multivalent ion solution at an applied pressure of 7 MPa and 21 °C.**

### 3.5. SEM

Figure 9 shows the SEM images taken on the surface of the MFI-type zeolite membrane after filtration testing with the multivalent ion solution. The filtration tested membrane was cleaned with HCl solution followed by DI water permeation prior to SEM measurements to remove weakly adsorbed material (including ions). The SEM image showed typical randomly orientated MFI-type zeolite crystals [7, 8, 11, 23], indicating that a zeolite membrane layer was grown on the surface of the Al<sub>2</sub>O<sub>3</sub> support. The zeolite crystals formed disorderly on the surface of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support and the surface of the Al<sub>2</sub>O<sub>3</sub> support was completely covered by MFI-type zeolite crystals. The size of the crystallites (~0.5  $\mu$ m) making up the zeolite membrane here was found to be smaller than that reported previously (e.g. ~2  $\mu$ m) [11]. This is likely to be due to the different synthesis conditions (e.g. different zeolite seeds) used for membrane preparation. It can also be seen from Figure 9 that the macrostructure of the zeolite membrane remained intact after filtration testing with the multivalent ion solution. However, some precipitate/scale was visible on the membrane surface after filtration and the spaces between the crystallites appear filled. Some scaling has also occurred on the MFI-type zeolite membrane surface after long term exposure to seawater at high temperatures [8]. Our previous ion infiltration study [18] confirmed that zeolites strongly interacted with ions (e.g. Fe<sup>3+</sup> and Al<sup>3+</sup>) present in ion solution and found that Fe<sup>3+</sup> was tightly bound with the zeolite material and was difficult to wash out even with HCl cleaning. This ion blocking effect was also evidenced by significant drops in gas permeation [18]. Interactions between the MFI-type zeolites and ions when exposed to seawater, a single salt solution (NaCl or KCl) or saline recycled wastewater were also observed in previous studies [7, 8, 11, 22, 23]. Membrane thickness (~9.8  $\mu$ m) measured from SEM images of a MFI-type zeolite membrane prepared in a similar way has been reported in our previous study [11].



**Fig. 9 SEM measured surface morphology of multivalent ion solution exposed MFI-type zeolite membrane.**

### *3.6. Implications of the practicalities of the application of MFI-type zeolite membranes to mining wastewaters*

Mining wastewaters typically contain high concentration of sulfate as well as other cations such as aluminium, calcium, potassium, sodium and magnesium, and can be strongly acid. Mining water treatment using membrane technology has recently become a rapidly emerging market. However, polymer membranes are limited in life due to the harsh conditions of mining effluents. Research and development of more robust membranes are, therefore, needed to enable more opportunities where current polymer membranes are limited. Here we show that MFI-type zeolite membranes may offer an alternative to polymer membranes for desalination of challenging mining wastewaters with low pH (e.g. 2), and containing ions of metals and sulphate. Good ion rejections were achieved in this study, and interestingly this was enhanced by the ion blocking effect from the interactions between ions present in ion complex model mining wastewater and zeolite materials. This study also confirmed that MFI-type zeolite membranes possess high chemical and thermal stability. While polymer membranes are not stable under heat (>50 °C), MFI-type zeolite membranes demonstrated improved salt rejecting performance at high temperatures (e.g. 70 °C). Despite the attractive virtues of zeolite membranes, there are still limitations and challenges in practice.



The first critical challenge refers to a significant improvement in fluxes of zeolite membranes in order to reduce capital cost and increase desalination capacity. As mentioned earlier, water fluxes of polymer membranes are much higher than those through zeolite membranes possibly due to the significant difference in membrane thickness (typical thickness of 3 – 10  $\mu\text{m}$  for zeolite membranes [2, 3, 11] is much thicker than commercial RO membranes (0.2  $\mu\text{m}$ ) [20, 21]) as membrane resistance to water transport is proportional to the dense surface layer thickness. While zeolite membrane thickness was mentioned as a potential reason for reduced flux, studies have shown that the flux of zeolite membranes could be improved by changing the hydrophobicity of the membrane [53] or through a single crystal zeolite nano-membrane [54]. For example, water flux of the zeolite membrane was increased by 10 times when the hydrophobicity of the membrane was decreased by adjusting the Si/Al ratio to 50 [19]. A recent molecular dynamics simulation study [54] also showed that a nanoscale single crystal zeolite (FAU or MFI-type) membrane with uniform pore size and high pore density can potentially achieve higher specific flux than state of the art polymer membranes.

In addition, the effects of trace cations present in wastewaters on the reliability of zeolite membranes should also be carefully considered. As mentioned earlier, a computational study has identified that multivalent cations cannot enter the intrinsic pores of zeolites, while monovalent cations (e.g.  $\text{K}^+$ ,  $\text{Na}^+$ ) can but are hindered by the inability for  $\text{Cl}^-$  to enter yielding a desalination effect [32]. Trace amounts of divalent cations (e.g.  $\text{Ca}^{2+}$ ) in seawater can occupy the grain boundaries of MFI-type zeolites [22] but are also blocked in defect free zeolite membranes. Trivalent cations (e.g.  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ ) can plug the large defect pores of MFI-type zeolites and this could potentially be utilised to inhibit non selective flux in pore defects but maintain water permeation through the intrinsic pores [18]. Although we did not see any negative effect or accumulation of Fe in our previous study on the application of MFI-type zeolite membrane for desalination of real municipal wastewater [11], the importance of interactions between these cations in trace amounts and the zeolite material cannot be underestimated as these interactions can alter the structure and porosity of zeolite material thus affecting membrane performance [8, 22-24]. Further study is needed to determine the effect of these cations on long term performance of MFI-type zeolite membranes.

While rejections (e.g. ~99% for  $\text{Fe}^{3+}$ , ~80 % for  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$ ) achieved in this study were reasonable for practical mining water desalination (for example, MacNaughton et al. [55]

reported 30 – 86% for  $\text{Mg}^{2+}$  and 28 – 85% for  $\text{SO}_4^{2-}$  on polymer NF membranes; Mullett et al. [56] reported > 94% for both  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  on polymer NF membranes), fluxes (e.g.  $\sim 0.3 \text{ L m}^{-2} \text{ h}^{-1}$ ), the flux of MFI-type membranes were significantly low compared to state of the art polymer membranes used for mining wastewater (e.g.  $16 – 25 \text{ L m}^{-2} \text{ h}^{-1}$  [55]). However, zeolite membranes exhibited unique effects in multivalent ion rich solution that could be further utilised in potential other applications such as niche desalination applications or sensors [57].

#### 4. Conclusion

A MFI-type zeolite membrane was prepared on a tubular  $\alpha$ -alumina substrate via the seeded and secondary hydrothermal growth method. The prepared MFI-type zeolite membrane was tested for filtration of an ion complex model of mining water containing  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  (TDS  $\sim 97,000 \text{ mg L}^{-1}$ , pH 2.03). The effects of applied pressure, temperature and acid cleaning on membrane performance were investigated. The results obtained from filtration performance testing showed that the prepared MFI-type zeolite membrane achieved good ion rejections for  $\text{Fe}^{3+}$  ( $\sim 99\%$ ),  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$  (both  $\sim 80\%$ ) but lower rejection for  $\text{Ca}^{2+}$  ( $\sim 50\%$ ) at 7 MPa and 21 °C. Higher operating temperature (e.g. 70 °C) resulted in higher ion rejection possibly due to the blockage of membrane pores by accelerated interactions between ions present in multivalent ion feed solution and zeolite materials. However, the blocking effect further contributed to some loss of membrane flux as observed for each temperature tested. Acid (1 M HCl) cleaning had no impact on ion rejection behaviour. The SEM results showed an intact membrane after exposure to multivalent ion solution. Regardless, the filtration performance of this range of ions at low pH had an interesting effect related to ion size and membrane charge.

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