Nanofiltration performance of SiO₂-ZrO₂ membranes in aqueous solutions at high temperatures

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Abstract

Nanofiltration performance at high temperatures was examined using SiO₂-ZrO₂ membranes fired at 200 and 550 °C. After SiO₂-ZrO₂ membranes were treated in water at 90 °C for 4 h, the water permeability (L_p) at 25 °C for both membranes increased approximately 3-fold and remained constant for as long as 100 h treatment, indicating stability in aqueous solutions as high as 90 °C. The increase in water permeability of membrane was ascribed to increased hydrophilicity and dissolution of silica into water at 90 °C. Molecular weight cut-offs (MWCOs) for SiO₂-ZrO₂ membrane fired at 550 °C did not change with treatment time (MWCOs = 300) while the MWCOs for SiO₂-ZrO₂ membrane fired at 200 °C increased from 240 to 300. SiO₂-ZrO₂ membranes fired at 550 °C showed higher hydrothermal stability than those fired at 200 °C.

The effect of temperature on SiO₂-ZrO₂ membrane performance was evaluated for nanofiltration at temperatures range of 25 to 90 °C. The rejection of glucose and maltose decreased with an increase in temperature for SiO₂-ZrO₂ membranes both fired at 200 and 550 °C, while the permeate flux increased. On the other hand, the temperature has no influence on rejection of raffinose, which was always larger than 95%.

Keywords: SiO₂-ZrO₂ membrane, nanofiltration, high temperature, hydrothermal stability

1. Introduction

Nanofiltration (NF) separation at high temperatures is desired for many industrial uses such as sugar processing in food industries and in textile and paper industries [1] where temperatures can reach 90 °C. In the literature [2], a high-temperature is defined as one that ranges between 50 and 95 °C in an aqueous solution and between 110 and 140 °C for extended periods under non-aqueous conditions. The advantages of using a high-temperature for separation are reduced pressure, operational cost savings and a sanitizing effect. However, only a limited number of studies have investigated NF performance under high temperatures. Pruksasri et al. [3] reported limitations of 60 °C for commercial polyethersulphone and polyamide NF membrane performance. One of the limitations of polymeric performances at high temperature is the thermal pore dilation which increases pore size with temperature [4]. A decrease in the rate of rejection and increased flux with an increasing temperature can be explained by the increase in membrane pore size and by the lower viscosity of a bulk solution [5]. Amar et al. [5, 6] studied the effect of temperature on the rejection of neutral (glycerin, arabinose, glucose, and sucrose) solutes by commercial polymeric membranes (Desal 5 DK, GE-Osmonics). The rejection for all neutral solutes decreased with increases in temperature because the effective pore radius increased slightly from 0.58 to 0.67 nm with increases in temperature from 22 to 50 °C. Polymeric NF membranes can be used in a limited temperature range, since many polymeric NF membranes (cellulose, polyamide and polysulfone, etc.) will soften, creep, and fail at 90 °C.

On the other hand, ceramic membranes such as alumina, titania, silica, and zirconia, etc. have shown excellent stability as well as chemical resistance at both acidic and basic pH, long lifetime and low thermal expansion under high temperatures. Tsuru et al. [7] reported TiO₂ membrane performance at temperatures ranging from 30 to 80 °C. In that study, the rejection of neutral solutes also decreased with an increase in temperature. Since pore size did not increase because of the rigid structure, the decreased rejection was ascribed to increased diffusivity inside the pores. Dobrak et al. [8] have reported that the rejection of solutes with titania and zirconia membranes did not change at temperatures ranging from 25 to 50 °C while the volume flux was

increased with temperature.

Silica comprises another class of materials for ceramic membranes. The advantage of silica membranes can be the controllability of pore sizes in a wide range from ultra-micropores (less than 0.7 nm) to mesopores (2-50 nm). The properties such as mechanical strength, phase structure, and pore structure have shown only a negligible change at high temperature with operating time [9]. However, due to the amorphous nature of silica material, the silica may undergo dissolution and/or densification when exposed to water, which can lead to a decrease in hydrothermal stability and a degraded separation performance [10-12]. This is a major problem when using silica membranes in an aqueous solution. Therefore, composite membranes of silica with various types of metal ions such as zirconia (ZrO_2), titania (TiO_2), aluminum (Al), etc., can improve the stability in aqueous solutions while simultaneously maintaining the advantage of pore-size controllability for SiO_2 [13, 14], which would allow the fabrication of stable nanofiltration membranes with low MWCOs. Tsuru et al. [15] reported that the water permeability of SiO_2 - ZrO_2 (9/1) NF membranes was decreased gradually during the first 2 days before reaching a stable value. The decrease in water flux was ascribed to the generation of OH groups that reduced the effective membrane pores.

Recently, we reported [16] that the water permeability of SiO_2 - ZrO_2 (5/5) NF membranes showed only a slight decrease during the initial 30 h, then reached stable values for as long as 100 h. Therefore, adding ZrO_2 into SiO_2 matrix is suggested to increase hydrothermal stability, which is quite important because the application of the membrane at high temperature is required in many separation processes, and the NF performance at high temperatures needs to be examined in detail.

In this study, nanoporous SiO_2 - ZrO_2 (molar ratio 5/5) membranes fired at 200 and 550 °C were treated in water at 90 °C in order to study thermal stability and evaluated nanofiltration performance. The temperature dependence of water permeability and rejection for SiO_2 - ZrO_2 membranes were examined in wide range temperatures from 25 to 90 °C.

2. Experimental

2.1 Preparation of SiO_2 - ZrO_2 colloidal sols and SiO_2 - ZrO_2 membranes

SiO₂-ZrO₂ composite colloidal sols with a molar ratio of 5/5 were prepared by the hydrolysis and condensation reactions of a tetraethoxysilane (TEOS) and zirconia-tetra-butoxide solution (ZTBO). SiO₂-ZrO₂ membranes were fabricated by coating SiO₂-ZrO₂ sols onto an α -Al₂O₃ support (average pore size 2.1 μ m; outer diameter 1 cm; length 10 cm), followed by calcinations under air at different firing temperatures. The pore sizes of SiO₂-ZrO₂ membranes, which were controlled by the colloidal sol sizes (as the top layer), were increased with an increase in the concentration of the SiO₂-ZrO₂ sol. Details of the preparation of SiO₂-ZrO₂ sols and SiO₂-ZrO₂ membranes were described in a previous report [16]. In this study, 19 and 35 nm SiO₂-ZrO₂ (5/5) sols and 12 nm SiO₂ sols were used to coat the top layer. SiO₂-ZrO₂ (5/5) membranes fired at 200 °C (sol 19 nm, M-200-1) and 550 °C (sol 19 nm, M-550-1 and sol 35 nm, M-550-2) and a SiO₂ membrane fired at 550 °C (sol 12 nm, M-550-3) were used in this study, and showed average pore sizes of 0.6, 0.7, 1.2, and 0.8 nm, respectively.

The silica and silica-zirconia powders were prepared by a quick-drying method [12] where the sols were dropped on a platinum plate at 180 °C, followed by firing at 200 and 550 °C. The solubility of the powders was tested in deionized water at pH of 7 through inductively coupled plasma (ICP, Seiko Instrument, SPS3000). Mixtures of 0.1 g of powders and 20 ml of deionized water were maintained at 25 and 90 °C for 4 h. After centrifuge at 5000 rpm for 15 min, the supernatant liquid was applied to ICP analysis, while the centrifuged powders were refilled with 20 ml of deionized water to repeat the dissolution experiment in water at 90 °C for 4 hr. This procedure was repeated by adding deionized water for 20 h.

2.2 Nanofiltration (NF) experiments

NF experiments were carried out using the experimental apparatus as described elsewhere [16] under vigorous agitation at 800 rpm with a magnetic stirrer in order to avoid any possibility of concentration polarization. The feed solution was pressurized at 1.0 MPa using a plunger pump and was recycled to the feed tank at an approximate flow rate of 20 ml/min. The solution temperature was controlled and monitored by a heating coil connected to a temperature-controlled water bath.

The solutes used for nanofiltration were neutral-organic with different molecular weights in aqueous solutions at concentrations of 500 ppm at pH of 7: isopropyl alcohol (60), glucose (180), maltose (342), and raffinose (504). It should be noted that the osmotic pressure for a solution of 500 ppm was negligible due to the low concentrations. The concentrations of feed and permeate were measured using a total organic carbon analyzer (Shimadzu, TOC-VE).

The experimental procedures for investigating the hydrothermal stability of SiO₂-ZrO₂ membranes in aqueous solution were as follows. First, the permeate flux and rejection of membranes were measured at 25 °C and then the membranes were treated in water at 90 °C for 4, 50 and 100 h in a separate flask where the water was freshened every 8 h. After hot-water treatment, the permeate flux and rejection were measured at 25 °C for each treatment. Finally, after treatment in water at 90 °C for 100 h, the effects of operating temperature (25, 50, 75, and 90 °C) on SiO₂-ZrO₂ nanofiltration membranes were determined at applied pressures from 0.25 to 1.00 MPa and then the temperature was decreased gradually back to 25 °C to recheck the permeate flux and the rejection. Each of the experimental data points represents the averaged value of 3 repeated measurements. The experimental errors in the permeate flux and the rejection were less than 3 and 1%, respectively.

2.3 Analysis of permeation properties

The permeate flux (J_v) through a membrane was formulated according to Kedem and Katchalsky [17], as follows:

$$J_v = L_p(\Delta P - \sigma\Delta\pi) \quad (1)$$

$$J_v = L_p\Delta P \quad (2)$$

where J_v is the permeate flux in m³/(m² s), L_p is the water permeability in m³/(m² s Pa), σ is the reflection coefficient, and ΔP and $\Delta\pi$ are the applied pressure difference and osmotic pressure differences in Pa. Due to the dilute solute concentration, Eq (1) was approximated to Eq. (2).

The solute permeability (B) through the membrane was calculated using the following

equations [18].

$$J_s = C_p J_v = C_p L_p \Delta P \quad (3)$$

$$J_s = B(C_f - C_p) + (1 - \sigma)\bar{C}J_v \quad (4)$$

where J_s is the solute flux in $\text{m}^3/(\text{m}^2 \text{ s})$, B is the solute permeability in m/s , C_p (mg/L) and C_f (mg/L) are the solute concentrations in the permeate and the feed, respectively, and $\bar{C}$ is the average concentration in the membrane pores. In this study, due to high rejection, the reflection coefficient ($\sigma = 1$) was assumed.

The rejection of solutes was defined as follows:

$$R = 1 - \frac{C_p}{C_f} \quad (5)$$

The activation energies (ΔE) of viscous flow were calculated based on the temperature dependence of the water viscosity. The temperature effect on water permeability was correlated using the Arrhenius equation [19], as follows:

$$L_p = (L_p)_0 \exp(-\Delta E(L_p) / RT) \quad (6)$$

$$L_p \mu = (L_p \mu)_0 \exp(-\Delta E(L_p \mu) / RT) \quad (7)$$

where ΔE is the activation energy in J/mol, μ is the viscosity in $\text{kg}/(\text{m s})$, R is the universal gas constant in J/(mol K) and T is the absolute temperature in K. The best-fit values of activation energy and the pre-exponential factor were estimated using linear regression. The activation energy error was less than 3%.

3. Results and discussions

3.1 Permeation properties at room temperature

3.1.1 Permeate flux and rejection of $\text{SiO}_2\text{-ZrO}_2$ membranes before hot-water treatment

Fig. 1 shows the permeate flux (J_v) and rejection of solutes (IPA, glucose, maltose and raffinose) as a function of molecular weights in the range of 60-500 g/mol. It should be noted that nanofiltration performances were stable for each measurement. Rejection of $\text{SiO}_2\text{-ZrO}_2$ membranes

fired at 200 and 550 °C increased with an increase in the molecular weight of solutes. The rejection of solutes using a SiO₂-ZrO₂ membrane fired at 200 °C was slightly higher than that fired at 550 °C because the average pore size of the SiO₂-ZrO₂ membrane fired at 200 °C (0.6 nm) was smaller than that fired at 550 °C (0.7 nm). The molecular weight cut-offs (MWCOs) of SiO₂-ZrO₂ membranes fired at 200 and 550 °C, which were defined at 90% rejection, were 240 and 300, respectively.

The permeate flux was not dependent on the types of solutes because of low concentration. A SiO₂-ZrO₂ membrane fired at 200 °C showed a higher permeate flux than that fired at 550 °C. This can be ascribed to the hydrophilicity/hydrophobicity of the membrane. Araki et al. [20] studied the effect of firing temperature of silica-zirconia (5/5) membranes for pervaporation. The water flux of IPA/water mixtures was reportedly reduced by increasing the firing temperatures due to a decrease in the number of silanol groups. In addition, the hydrophilicity/hydrophobicity of the inner surface of nanoporous SiO₂-ZrO₂ membranes was qualitatively evaluated based on contact angles that were determined by nanoporometry measured using water and hexane vapor. The averages of the contact angles for SiO₂-ZrO₂ membranes fired at 200 and 550 °C were 21 and 36°, respectively [16], indicating that higher firing temperatures lead to more hydrophobic pores in SiO₂-ZrO₂ membranes. Moreover, the effect of hydrophilicity/hydrophobicity was further examined by feeding of water and methanol. Fig. 2 shows the permeate flux (J_v) of water for SiO₂-ZrO₂ membrane (pore size of 1.2 nm, M-550-2) before/after the feeding of methanol. The permeate flux of SiO₂-ZrO₂ membrane just after the membrane fabrication was stable at $9.0 \times 10^{-6} \text{ m}^3 / (\text{m}^2 \text{ s})$. This membrane was removed from the nanofiltration cell, washed with methanol, and set in another nanofiltration cell filled with methanol. After measurement of the methanol permeation for 5 h, the membrane was taken out and rinsed with pure water, then set back into the nanofiltration cell filled with water, followed by measurement of the water flux. During the experiment the membrane was treated under wet conditions so as to exchange solvent continuously. The permeate flux of the SiO₂-ZrO₂ membrane after the feeding of methanol increased from 9.0×10^{-6} to $11.5 \times 10^{-6} \text{ m}^3 / (\text{m}^2 \text{ s})$. This also suggests that the hydrophobic portions, which were not available for water permeation, were wetted by the methanol due to the low surface tension and amphiphilicity, and it also suggests that all parts of the

SiO₂-ZrO₂ membranes contributed to the increase in permeate flux. It should be noted that the permeate flux of methanol was much lower than that of water probably due to pore size reduction by the adsorbed methanol on the membrane surface and/or a plugging of the pores by methanol.

Fig. 1 Permeate flux (J_v) at 25 °C, $\Delta P = 1.0$ MPa and rejection of solutes as a function of molecular weights for SiO₂-ZrO₂ membrane fired at 200 °C (M-200-1) and 550 °C (M-550-1).

Fig. 2 Permeate flux (J_v) of water and methanol at 25 °C, $\Delta P = 1$ MPa for SiO₂-ZrO₂ membrane fired at 550 °C (average pore size of 1.2 nm, M-550-2).

3.1.2 Permeate flux and rejection of SiO₂-ZrO₂ membranes after hot-water treatment

After confirming nanofiltration performances at 25 °C, SiO₂-ZrO₂ membranes were subjected to hot-water treatment at 90 °C in order to study the hydrothermal stability and nanofiltration performance of SiO₂-ZrO₂ membranes. Fig. 3 shows the permeate flux (J_v) at 25 °C and the rejection of glucose by SiO₂-ZrO₂ membranes fired at 200 and 550 °C and SiO₂ membrane fired at 550 °C as a function of treatment time. After the SiO₂-ZrO₂ membranes were treated in hot water (90 °C) for 4 h, the permeate flux at 25 °C for the membranes fired at both 200 and 550 °C was increased dramatically from 3.1×10^{-6} to 8.9×10^{-6} m³/(m² s) and from 2.0×10^{-6} to 4.8×10^{-6} m³/(m² s), respectively. After the initial 4 h, the permeate flux of the SiO₂-ZrO₂ membranes fired at both 200 and 550 °C showed stable values for as long as 100 h. The rejection of glucose was decreased from 80 to 60% for SiO₂-ZrO₂ membrane fired at 200 °C after treatment in water at 90 °C for 4 h and reached a stable value of 60% for 100 h. On the other hand, the rejection of glucose by SiO₂-ZrO₂ membrane fired at 550 °C was almost stable (75%) for 100 h. Furthermore, the permeate flux of SiO₂ membrane increased dramatically during 25 h treatment while the rejection of glucose decreased rapidly from 80 to 10%. The decrease in the rejection of glucose can be explained by increases in the size of the membrane pores due to the dissolution of Si into water at 90 °C, which is suggested in Fig. 5. Therefore, SiO₂-ZrO₂ membrane was more hydrothermally stable than SiO₂ membrane.

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Fig. 3 Permeate flux (J_v) at 25 °C, $\Delta P=1$ MPa and rejection of glucose as a function of time course after treatment in water at 90 °C for $\text{SiO}_2\text{-ZrO}_2$ (5/5) membranes fired at 200 °C (M-200-1), 550 °C (M-550-1) and SiO_2 membrane fired at 550 °C (M-550-3).

Fig. 4 shows the rejection of solutes and permeate flux as a function of molecular weights for $\text{SiO}_2\text{-ZrO}_2$ membranes. After treatment in water at 90 °C for 4 h, the permeate flux (J_v) at 25 °C of $\text{SiO}_2\text{-ZrO}_2$ membrane fired at 200 °C showed a greater increase than those fired at 550 °C, and these values remained stable for as long as 100 h. The rejections of isopropyl alcohol (MW = 60) and glucose (MW = 180) decreased for $\text{SiO}_2\text{-ZrO}_2$ membrane fired at 200 °C while rates for the rejection of maltose (MW = 342) and raffinose (MW = 504) were constant for 100 h. The MWCOs of $\text{SiO}_2\text{-ZrO}_2$ membrane fired at 200 °C increased from 240 to 300, while those of $\text{SiO}_2\text{-ZrO}_2$ membrane fired at 550 °C was constant at 300. Therefore, $\text{SiO}_2\text{-ZrO}_2$ membrane fired at 550 °C was hydrothermally more stable in water at 90 °C than those fired at 200 °C.

Fig. 4 Rejection of solutes and permeate flux (J_v) at $\Delta P = 1$ MPa, 25 °C as function of molecular weights after treatment in water at 90 °C for 4, 50 and 100 h for SiO₂-ZrO₂ membranes; (a) fired at 200 °C, (b) fired at 550 °C

The increase in permeate flux after treatment in water at 90 °C was examined by measuring the dissolution of Si into water, as shown in Fig. 5. The solubility of Si in water at 25 °C for SiO₂ powders fired at 200 and 550 °C was approximately 6 ppm, which was much higher than that for the Si in SiO₂-ZrO₂ (5/5) powders fired at 200 and 550 °C at 0.5 ppm. At 90 °C (4 h), however, the solubility of Si for SiO₂ powders increased to approximately 11 ppm, while that of SiO₂-ZrO₂ powders increased to only 1.2 ppm (fired at 550 °C) and 2.5 ppm (fired at 200 °C), confirming the increased stability in water that was accomplished by adding ZrO₂ into the SiO₂ matrix. Therefore, adding ZrO₂ content about 50 mol% into the SiO₂ leads to higher thermal stability. After repeating the dissolution experiment of the powders in water at 90 °C for 8-20 h by refilling with fresh water, the solubility of Si was decreased even further. It is interesting that SiO₂-ZrO₂ powder fired at 550 °C showed a solubility of zero in water at 90 °C after treated powders for 16 h while the SiO₂-ZrO₂ powder fired at 200 °C was dissolved at a rate of approximately 1.5 ppm. This strongly suggests

that $\text{SiO}_2\text{-ZrO}_2$ membrane fired at 550 °C is more stable in hot water than that fired at 200 °C. On the other hand, the solubilities of Zr in water at 25 and 90 °C were negligible (approximately 0.05-0.10 ppm) for both $\text{SiO}_2\text{-ZrO}_2$ powders fired at 200 and 550 °C. This can explain why the permeate flux for $\text{SiO}_2\text{-ZrO}_2$ membrane fired at 200 °C increased more largely than that fired at 550 °C while the rejection of glucose decreased, that is, dissolution of Si into water enlarged membrane pore sizes for permeation.

Fig. 5 Solubility of Si in water for SiO_2 and $\text{SiO}_2\text{-ZrO}_2$ (5/5) powders fired at 200 and 550 °C as a function of treatment time in water at 90 °C.

Additionally, another reason for the increased flux can be ascribed to an increase in hydrophilicity. As schematically shown in Fig. 6, OH groups were formed on the surface of the $\text{SiO}_2\text{-ZrO}_2$ membranes after contact with water at 90 °C. The formation of the OH groups had two effects: increased hydrophilicity, which is favorable for increased flux, and narrowed pore sizes, which may decrease flux and increase rejection [12, 21, 22]. Nanofiltration performance after hot-water treatment could be determined by the balance of the two effects: hydrophilicity and pore-narrowing. Therefore, after treatment of the membrane in water at 90 °C, the permeate flux of $\text{SiO}_2\text{-ZrO}_2$ membranes was increased due to the dissolution of Si and to an increase in hydrophilicity.

Fig. 6 Schematic of $\text{SiO}_2\text{-ZrO}_2$ membrane pores after treatment in water at 90 °C.

Fig. 7 shows the surface for $\text{SiO}_2\text{-ZrO}_2$ membranes fired at 200 and 550 °C at a magnification of 500. The pore sizes on the surfaces of the membranes were too small to be observed by SEM. However, the surfaces of $\text{SiO}_2\text{-ZrO}_2$ membranes fired at 200 and 550 °C were not changed significantly after treatment in water at 90 °C for as long as 100 h. This indicates that $\text{SiO}_2\text{-ZrO}_2$ (5/5) membranes show high thermal stability in hot water.

Fired at 200 °C

Fired at 550 °C

Fig. 7 SEM photograph of $\text{SiO}_2\text{-ZrO}_2$ membranes fired at 200 °C (a, c) and 550 °C (b, d); (a, b) before treatment membranes and (c, d) after treatment membranes in water at 90 °C for 100 h.

3.2 Permeation properties at high temperatures

3.2.1 Effect of temperature on water permeability

Fig. 8 shows the permeate flux (J_v) of pure water through SiO₂-ZrO₂ membranes fired at 200 and 550 °C as a function of applied pressure. The permeate flux increased linearly with applied pressure and also increased with increases in temperature from 25 to 90 °C, because of a reduction in the viscosity of the water. The permeate flux of the SiO₂-ZrO₂ membranes fired at 200 and 550 °C was increased 4-fold for feed temperatures ranging 25 to 90 °C, which suggests preferable operation at high temperatures. According to the viscous flow mechanism, the water permeability (L_p), which can be obtained by the slope between the permeate flux (J_v) and the applied pressure (ΔP) through a porous membrane, is formulated according to the following Hagen-Poiseuille equation [7]:

$$L_p = \frac{J_v}{\Delta P} = \frac{r_p^2 A_k}{8\mu\Delta x} \quad (8)$$

where r_p is the effective pore size, Δx is the membrane thickness, A_k is the membrane porosity, and μ is the viscosity of the solution.

The viscous flow mechanism, $L_p\mu$, is defined as water permeability (L_p) multiplied by viscosity (μ) and should be constant as shown by the structural parameters of the membrane in Eq. 8, where r_p , A_k and Δx remained constant irrespective of the permeation temperature. As shown in Fig. 9, the values for $L_p\mu$ of SiO₂-ZrO₂ membranes fired at 200 and 550 °C were not constant and increased slightly with temperatures ranging from 25 to 90 °C. This is consistent with previous reports that $L_p\mu$ was increased with temperature [7, 23, 24]. The reason for this can be explained by the fact that the viscosity of water inside nanopores was different from the viscous flow which was calculated using bulk viscosity. Another reason could be that the thickness of the adsorbed water in a membrane pore decreases with temperature. Table 1 summarizes the observed activation energy (ΔE) values of L_p and $L_p\mu$ for SiO₂-ZrO₂ membranes fired at 200 and 550 °C. The ΔE (L_p) and ΔE ($L_p\mu$) for SiO₂-ZrO₂ membranes fired at 200 and 550 °C had similar values because they had approximately the same pore sizes, which ranged from 0.6-0.7 nm. Reports of the activation energy

of L_p values for titania membranes with average pore sizes of 0.7, 1.0 and 2.5 nm were 22.7, 19.7 and 18.0 kJ/mol, respectively, and the activation energy of $L_p\mu$ values were 8.2, 5.1 and 3.5 kJ/mol, respectively, indicating that the activation energy of L_p and $L_p\mu$ was increased with a decrease in the pore diameter [7, 23, 25]. The activation energies of SiO₂-ZrO₂ membranes with pore sizes ranging from 0.6-0.7 nm were consistent with those of titania membranes, which shows that the pore sizes of nanoporous SiO₂-ZrO₂ and TiO₂ membranes are crucial in determining activation energies. In addition, it can be concluded that the water permeation mechanism through nanoporous membrane is different from the viscous flow.

Fig. 8 Permeate flux (J_v) as function of pressure (ΔP) with different temperatures for SiO₂-ZrO₂ membranes; (a) fired at 200 °C, (b) fired at 550 °C (pure water).

Fig. 9 Viscosity-corrected water permeability, $L_p\mu$ as function of temperature for SiO₂-ZrO₂ membranes fired at 200 and 550 °C.

Table 1

Activation energy of L_p and $L_p\mu$ for SiO₂-ZrO₂ membranes fired at 200 and 550 °C

Activation energy [kJ mol ⁻¹]	SiO ₂ -ZrO ₂ membranes	
	Fired at 200 °C	Fired at 550 °C
$\Delta E (L_p)$	22.2	22.3
$\Delta E (L_p\mu)$	7.8	7.9

3.2.2 Effect of temperature on the rejection of solutes

Nanofiltration performances were evaluated by the permeate flux (J_v) and the rejection at an applied pressure of 0.25 MPa using neutral solutes with a variety of molecular weights. Fig. 10 shows the time course of permeate flux and rejection of solutes at temperatures ranging from 25 to 90 °C. The values for both permeate flux and rejections were stable for 4 h during the measurement at each temperature. The J_v increased with an increase in the operating temperature (25-90 °C) for SiO₂-ZrO₂ membranes fired at 200 and 550 °C while the rejection of glucose decreased dramatically and the rejection of maltose decreased gradually. Interestingly, the rejection of raffinose for SiO₂-ZrO₂ membranes both fired at 200 and 550 °C seems to have been unchanged, and was higher than 97% for temperatures range from 25 to 90 °C. After the feed temperature was decreased gradually back to 25 °C, both the permeate flux and the rejection of solutes (open key) returned to the initial values. This indicates that the SiO₂-ZrO₂ membranes showed excellent hydrothermal stability in water at 90 °C. As shown in Fig. 11, the MWCOs at 90% rejection at 25, 50, 75 and 90 °C were 270, 320, 350 and 380, respectively, for SiO₂-ZrO₂ membrane fired at 200 °C, and were 300, 320, 340 and 370, respectively, for SiO₂-ZrO₂ membrane fired at 550 °C.

Fig. 10 Time course for permeate flux (J_v) and rejection of solutes at applied pressure 0.25 MPa at different temperatures (25-90 °C) for $\text{SiO}_2\text{-ZrO}_2$ membranes (open key: regeneration temperature at 25 °C); (a) fired at 200 °C (M-200-1), (b) fired at 550 °C (M-550-1).

Fig. 11 The rejection of solutes at applied pressure 0.25 MPa as a function of molecular weights for $\text{SiO}_2\text{-ZrO}_2$ membranes; (a) fired at 200 °C (M-200-1), (b) fired at 550 °C (M-550-1).

Fig. 12 shows the rejection of glucose, water permeability (L_p) and solute permeability (B) for $\text{SiO}_2\text{-ZrO}_2$ membranes as a function of different applied pressures (0.25, 0.50, 0.75 and 1.00 MPa) at different operating temperatures (25, 50, 75 and 90 °C). At a constant permeation temperature, the rejection of glucose for $\text{SiO}_2\text{-ZrO}_2$ membranes fired at both 200 and 550 °C

increased with an increase in applied pressure, which is a typical tendency for pressure-driven membranes (RO, NF and UF), while the rejection decreased with temperature increases from 25 to 90 °C. An increase in the water permeability and a decrease in the rejection of solutes with temperature for nanofiltration can be explained using the Spiegler-Kedem theory. This theory assumes that a solute is simultaneously transported by the diffusion of the solutes and convective solvent flow through the pores. Rejections always increase with increases in flux due to the limited contribution of the diffusion to the solute flux. When the convective solvent drag dominates a negligible contribution from the solute diffusion, the rejection remains constant. Therefore, the diffusion and convection of solutes through membrane pore affect rejections [5, 7, 8].

The L_p , which was obtained by $J_v/\Delta P$, was constant irrespective of applied pressure, confirming a negligible osmotic pressure (Eq. (1)). Solute permeability (B) was obtained using Eqs. (3) and (4), and also showed constant values irrespective of ΔP at permeation temperatures from 25 to 90 °C. This confirms the applicability of the simple permeation model, as shown by Eqs. (1) - (3). B was increased with temperature, which demonstrated its temperature dependency. This is consistent with previous reports regarding the temperature dependence of neutral solutes [7, 23].

Table 2 summarizes the L_p , R and activation energies of B and L_p for SiO₂-ZrO₂ membranes fired at 200 and 550 °C. The activation energy of solute permeability, $\Delta E (B)$, indicates the dependency of solute permeation on temperature. The larger $\Delta E (B)$, the more solute flux increased with temperature while the activation energy of water permeability, $\Delta E (L_p)$, did not change with an increase in the molecular weight of solutes. Interestingly, $\Delta E (B)$ was much higher than $\Delta E (L_p)$, which can explain the lowered rejection at high temperature, higher diffusivity of solutes decreased rejection.

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Fig. 12 Solute permeability (B), water permeability (L_p) and rejection of glucose for SiO₂-ZrO₂ membranes fired at (a) 200 °C (M-200-1) and (b) 550 °C (M-550-1) as a function of applied pressure at different operating temperatures 25, 50, 75 and 90 °C.

Table 2 Summary of SiO₂-ZrO₂ membrane parameters after treatment in water at 90 °C for 100 h

Membrane	Solutes	Temperature [°C]	L_p [10 ⁻¹² m ³ /(m ² s Pa)]	R^* [%]	$\Delta E (B)$ [kJ/mol]	$\Delta E (L_p)$ [kJ/mol]
SiO ₂ -ZrO ₂ fired at 200 °C	glucose	25	8.8	75	42.4	20.8
		90	31.7	32		
	maltose	25	8.9	95	39.7	21.1
		90	31.8	85		
SiO ₂ -ZrO ₂ fired at 550 °C	glucose	25	8.7	98	29.2	21.2
		90	31.0	95		
	maltose	25	4.5	72	38.8	22.2
		90	16.3	42		
	maltose	25	4.8	93	34.9	23.3
		90	16.4	86		
	raffinose	25	4.7	97	29.3	23.2
		90	16.6	95		

*Rejection (*R*) at applied pressure at 0.25 MPa

3.3 Comparison of NF performance

For comparison, the performances of different ceramic nanofiltration membranes are summarized in Table 3 and shown in Fig. 13. γ -Al₂O₃, TiO₂, ZrO₂ and SiO₂-ZrO₂ (9/1) membranes showed MWCOs ranging from 200 to 1000, which is within the normal range for nanofiltration (NF) membranes (in general, MWCOs of 200-1000) [26, 27]. SiO₂-ZrO₂ (9/1) membranes, the pore size of which can be controlled in a wide range from 0.7 to 3.0 nm, showed MWCOs of 200-1000, but SiO₂-ZrO₂ (9/1) membranes were unstable in aqueous solution [15]. In this work, SiO₂-ZrO₂ (5/5) membranes were prepared to study hydrothermal stability and nanofiltration performance. After hot-water treatment of membranes for 100 h, the water permeability at 25 °C for SiO₂-ZrO₂ (5/5) membranes increased from 3.1×10^{-12} to 8.8×10^{-12} m³/ (m² s Pa) for membrane fired at 200 °C and increased from 2.0×10^{-12} to 4.8×10^{-12} m³/ (m² s Pa) for membrane fired at 550 °C. It is interesting, that SiO₂-ZrO₂ (5/5) membranes fired at 550 °C and treated with hot water showed constant MWCOs of 300, irrespective of hot-water treatment. NF membranes with high performance are expected to show a high level of water permeability and low MWCO levels. As shown in Fig. 13, SiO₂-ZrO₂ (5/5) membranes fired at 200 and 550 °C showed nanofiltration with small MWCO levels and high levels of water permeability, which is crucial for developing improved nanofiltration membranes. Based on Fig. 13, we can conclude that SiO₂-ZrO₂ membranes fired at 550 °C showed excellent hydrothermal stability and high performance in water at 90 °C. Additionally, SiO₂-ZrO₂ (5/5) membranes fired at 200 and 550 °C, which can be operated at temperatures as high as 90 °C, showed MWCOs that ranged from 240 to 380 and from 300 to 370, respectively.

Table 3

Comparison of the performances of different ceramic nanofiltration membranes

Membrane	Temperature [°C]	Water permeability [$10^{-12} \text{ m}^3 / (\text{m}^2 \text{ s Pa})$]	MWCOs [g/ mol]	Reference
$\gamma\text{-Al}_2\text{O}_3$	25	3.0	380	[28]
		3.8	450	[28]
		6.3	900	[29]
TiO_2	25	1.8	890	[30]
		2.0	500	[31]
		11.0	600	[7]
		10.8	200	[32]
		27.7	250	[33]
ZrO_2	25	0.5	350	[34]
		6.3	290	[35]
$\text{SiO}_2\text{-ZrO}_2$ (9/1)	25	1.5	200	[15]
		6.6	500	
		14.6	1000	
$\text{SiO}_2\text{-ZrO}_2$ (5/5)	25	3.1, 8.8*	240, 300*	This work
(fired 200 °C)	50	13.8*	320*	This work
	75	25.1*	350*	This work
	90	31.5*	380*	This work
$\text{SiO}_2\text{-ZrO}_2$ (5/5)	25	2.0, 4.8*	300, 300*	This work
(fired 550 °C)	50	6.9*	320*	This work
	75	12.4*	340*	This work
	90	16.5*	370*	This work

*After treatment in water at 90 °C for 100 h

Fig. 13 The trade-offs in molecular weight cut-offs (MWCOs) at 25 °C as a function of the water permeability (L_p) for ceramic nanofiltration membranes (open key: after treatment in water at 90 °C).

4. Conclusions

SiO₂-ZrO₂ membranes were evaluated for nanofiltration performance at high temperatures. After treatment of the membranes in water up to 90 °C for 4 h, the water permeability of SiO₂-ZrO₂ membranes fired at 200 and 550 °C was increased dramatically from 3.1×10^{-12} to 8.8×10^{-12} m³/ (m² s Pa) and 2.0×10^{-12} to 4.8×10^{-12} m³/ (m² s Pa), respectively, under an operating temperature of 25 °C and reached stable values for as long as 100 h of treatment in water at 90 °C. The increased water permeabilities were due to the dissolution of silica into water at 90 °C and to an increase in the hydrophilicity. On the other hand, the rejection of glucose for a SiO₂-ZrO₂ membrane fired at 200 °C was decreased from 80 to 60%, while that for a SiO₂-ZrO₂ membrane fired at 550 °C showed excellent hydrothermal stability in water at 90 °C (rejection of solutes did not change).

The membrane transport mechanism for water can be expressed using the activation energy of L_p and $L_p\mu$, which showed similar values for SiO₂-ZrO₂ membranes fired at 200 and 550 °C because they had approximately the same average pore size. The effect of temperature on SiO₂-ZrO₂ membrane performance was examined according to MWCOs at temperatures ranging from 25 to 90 °C, which increased in range from approximately 300 to 380. On the other hand, the water permeability for the SiO₂-ZrO₂ membranes was increased with an increase in temperature, while the rejections of glucose and maltose were decreased due to an increase in solute permeability (B) caused by diffusion.

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Graphical abstract