Silica Membranes for Wetland Saline Water Desalination: Performance and Long Term Stability

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Abstract. In this study, silica thin film pH=6 (precursor TEOS:tetraethyl orthosilicate) developed from sol gel process and deposited (2 layers) directly onto alumina substrate(tubular support with 100 nm pore size) without depositing interlayer (interlayer-free).Then, the desalination process via pervaporation was applied to test the membranes performance using artificial saline water and wetland saline water. Results show the decrease of water flux (1.9 to 1.43 kg m⁻² h⁻¹) and salt rejection (97 to 95%) when using artificial salty water (0-7.5 wt%) and the long-term stability of silica membrane was stable at 1.7 kg m⁻² h⁻¹ for over 100 hours when using wetland saline water as a feed.

Keywords: silica membranes; desalination; sol gel process, water flux and salt rejection.

1. Introduction

Literature reported that water is the basic needs of human living. Unfortunately, there is only 3% of water available as fresh water, the remaining 97% of water contain salt. The World Health Organization (WHO) also said that there is more than 15% of the world's population does not have access to drinking water. One way to overcome the problem of accessing clean water is by applying the appropriate membrane technology. Water desalination is one part of the technology to adapt. In addition, desalination has an environmentally friendly, energy-efficient, low operating cost and minimal use of chemicals. So this method becomes an interesting option for further investigation. Based on solubility or salt content in water, salty water can be grouped into three types (brackish water, saline water and brine water). Fresh water, brackish water, saline (sea) water and brine water has a salinity of less than 0.5, between 0.5 – 17, 35 and above 35 ppt (part per thousand), respectively. Desalination is a process for reducing minerals dissolved in seawater into fresh water with a maximum concentration of 500 ppm. Membrane technology is a part of desalination process that mostly chosen due to its high efficiency, ease of operation, energy-saving and non-chemical. This technology has been widely applied to various processes such as gas separation, pervaporation, ion exchange membranes, membrane reactors and wastewater treatment. This technology has also several advantages, such as: enable to separate within specific chemical molecules, enable to operate at low temperatures, low energy consumption and friendly environment. In addition, separation technique using membranes can run continuously and do not require much energy and the addition of chemicals (coagulant and flocculants). Sol gel process is a simple way to separate the molecules.

Besides applied for water desalination, pervaporation process is also applied to recover liquid organic compounds into steam by reducing pressure on the permeate side. It then also be used for the separation of azeotropic fluid mixture, preferring polymeric membranes, very low water concentration and mixing boiling point adjacent. Our previous research reported a fabrication of pure silica membranes using CTP (Conventional Thermal Process) method. When compare to this study, the CTP method takes a longer time to produce every one layer of silica membrane. However, in this research has applied RTP (Rapid Thermal Process) method. This method is very simple and low cost due to the time required to fabricate silica membrane is much shorter and save lots of energy. It is because during calcination process, there was no ramping rates applied. This research aims to investigate the performance (water flux and salt rejection) and long term performance of pure silica membrane using RTP method of calcination.
2. Methodology

a. Silica sols and Membrane Thin Film Synthesis and Fabrications

Silica sols were synthesized from a two-step sol gel process employing acid and base as catalysts (followed our previous work). Tetraethyl orthosilicate (TEOS) was added drop-wise into ethanol (EtOH) solution and stirred for 5 min in ice bath condition at 0 °C to avoid partial hydrolysis followed by the addition of diluted nitric acid (0.0008 M HNO₃). The sol mixture was refluxed for 1 hours at 50 °C with stirring to achieve a complete hydrolysis of the alkoxy groups. Ammonia solution (NH₃) diluted in ethanol was added drop wise into sol mixture to commence the condensation reaction and reflux was continued for another 2 hours to obtain the resultant sol. Silica sols solution was then dried in a temperature controlled oven at 60 °C for 24 hours to obtain the dried gel for xerogel characterization. The final molar ratios of the sol (TEOS:EtOH:HNO₃:H₂O:NH₃) were calculated to be 1:38:0.00078:5:0.003.

Furthermore, silica sol solution (thin membrane films) were coated on macroporous alumina substrates (α-Al₂O₃ tubular support, pore size ≈ 100 nm) via a dip-coating process with a dwell time of 2 min and a dipping and withdrawal rate of 10 and 5 cm min⁻¹, respectively. After the deposition of each layer, the membrane layer was dried and calcined in a furnace at 600 °C for 1 hours. Repeat this cycle of dip-coating and calcination until two number of silica membrane layers.

b. Silica Xerogel and Membrane Characterisation

The characterization of the silica xerogel was performed to determine the physical and chemical properties of dried sol. Several equipment were employed:
- FTIR (Fourier Transform Infra-Red) is used to determine functional groups in silica sol. FTIR spectra data were collected from FTIR type Bruker Alpha. Instrument type: alpha sample compartment RT-DLaTGS accessory: ATR platinum Diamond 1 Relf. The spectra were collected from a total of 30 scans ranging between wavelengths 500-4000 cm⁻¹. IR spectra were deconvoluted by using Fityk software with an approximately 10% error. Gaussian curve was chosen to fit the peaks. HWHM (the half width half max) values were consistently fixed for the same deconvoluted peaks.

- SEM (Scanning Electron Microscopy), SEM EVO® MA 10 is to know the morphology: the surface structure and thickness of the silica membrane.

c. Membrane Desalination and Long-Term Stability

The first step is to prepare a feed solution at 0.3; 1; 3.5% of saline water. Each feed solution was placed into the feed tank. Then connect the coldtrap and assemble in the classical pervaporation set-up as shown in Figure 1. The dead-end mode of tubular silica membrane was set (one of end of pipe was blocked and the other was connected to coldtrap and vacuum pump. Membrane was immersed into feed solution and then the pervaporation was started in every 20 minutes. The separated solution will evaporate and flow through pore size of membrane and collected in the cold trap. The evaporated molecules was then condensed in the cold trap by immersing coldtrap into ice bath. The following step is to calculate the water flux and measure the salt rejection using a conductivity meter. Then calculations of the water flux and salt rejection were repeated three times in every measurement.
Figure 1. Desalination rig via classical pervaporation set up.

The water flux, \( F \) (kg m\(^{-2}\) h\(^{-1}\)), was determined based on the Equation \( F = \frac{m}{A \cdot \Delta t} \), where \( m \) is the mass of permeate (kg) retained in the cold trap, \( A \) is the surface-active area (m\(^2\)) and \( \Delta t \) is the time measurement (h). The salt rejection, \( R \) (%), was calculated as \( R = \frac{(C_f - C_p)}{C_f} \times 100\% \), where \( C_f \) and \( C_p \) are the feed and permeate concentrations of salt (wt %). Lastly, long term membrane performance for hydrostability was conducted in a wetland saline water at room temperature (+/- 26 °C, wetland saline water was taken during rainy season).

3. Results And Discussion

a. Silica Sol

This sol-gel method is a sole-forming process by reacting precursors and ethanol with acid and base as catalysts. During the process, there are several stages of the process; (i) hydrolysis, (ii) condensation of alcohol and (iii) water condensation. In the first 1 hour of reflux, the silanol (Si - OH) bridges under acidic conditions (pH~4) starts to form during hydrolysis process. It is due to the TEOS as a precursor are dissolved into ethanol and hydrolyzed by addition of water and nitric acid as a catalyst. This hydrolysis process replaces the alkoxy group (-OR) with the hydroxy group (-OH). During the hydrolysis process, the (-OR) group of TEOS will react with water molecules, thus forming silanol. The reactions can be seen in the following equation.

\[
\text{Si} – \text{OR} + \text{H}_2\text{O} \leftrightarrow \text{Si} – \text{OH} + \text{ROH}
\]

In the second reflux, the siloxane (Si-O-Si) was then formed by the condensation process. The result of the hydrolysis reaction (Si-OH) react with TEOS and with the help of the basic catalyst (ammonia) resulting in condensation of the alcohol and the resulting siloxane. The addition of this ammonia will increase the pH value greater than 4. In this reaction, the excessive ethanol reforms of the siloxane bridges by the reaction of water and alcohol condensation. The reaction occurred can be seen in the following equation[17].

\[
\text{Si} – \text{OR} + \text{HO} – \text{Si} \leftrightarrow \text{Si} – \text{O} – \text{Si} + \text{ROH}
\]

\[
\text{Si} – \text{OH} + \text{HO} – \text{Si} \leftrightarrow \text{Si} – \text{O} – \text{Si} + \text{H}_2\text{O}
\]

b. Characterization of Xerogel

FTIR (Fourier Transform Infra Red) analysis is used to determine silanol and siloxane groups in silica structures. The selective peaks of FTIR analysis can be seen in Figure 2, as follow.

Figure 2 indicates the presence of siloxane (Si-O-Si) groups at wavelength 1082 cm\(^{-1}\) and 800 cm\(^{-1}\). Then another peak was found that it was a silanol group (Si-OH) at a wavelength of 1001 cm\(^{-1}\). It is clearly seen that the silanol concentration is much smaller than the siloxane concentration. This is because silanol groups tend to form smaller pore size (microporous). In reverse to siloxane groups, these groups prefer to form meso and macroporous. The combination between micro and mesoporous structures affect great separation between water and salt molecules. And this pattern brings the membranes performance become excellent. Similar to our previous work called bottle neck [18]. In addition, siloxane can strengthen the membrane structures.
Figure 2. (a) FTIR spectra of the calcined silica xerogels

Figure 3. Cross-section of SEM image of silica membrane

From this Figure, the thickness of the silica membrane estimated to be ~1μm. It is thicker than CTP techniques of calcination form our previous work (around 470 nm) [9]. This difference is caused by the process of calcination on RTP conducted in this study is shorter than the CTP method conducted by [9]. In addition, the RTP process does not use heating rate and cooling rate as it does in the CTP method. This causes the solvent in sol thin film does not evaporate completely during
calcination process. Therefore, the solvent trapped in the thin film of membrane layer still continue on doing water and alcohol condensation and affect to the silica structure. This is what causes the membrane layer to become thicker. It is also due to the fact that when the calcination process is carried out at high temperatures, the solvent in the silica sol (thin film) lining on the imperfect membrane support evaporates due to the sudden rise in temperature during calcination process.

d. Membrane Performance

Performance of silica membrane in desalination process can be seen from the value of salt rejection. In this study, the membrane will be tested at different feed concentrations, from 0% (fresh water), 0.3 - 1% (brackish water), 3.5% (sea water) and 5 - 15% (brine water).

The water flux and salt rejection of the membrane were 2.1 kg m\(^{-2}\) h\(^{-1}\) and 99.51% respectively for 0.3 wt% salt water as a feed. From these results can be concluded that the greater the concentration of feeds, the lower the water flux as well as salt rejection. It is due to the higher feed solution the higher salt molecules in the solution. Therefore, those molecules block the pores and create the flow of water molecules pass through the membranes become much slower. In other way, the membrane performance due to the polarization effect. When feed with high salt concentration through the membrane, salt particles will cover the membrane pores so that water will be difficult to pass through the membrane. Therefore, this salt polarization effect will reduce the thrust on the membrane.

In the research [9], with the CTP (Conventional Thermal Process) method, the highest water flux and salt rejection values were produced at 0.3% feed concentration of 9.5 kg m\(^{-2}\) h\(^{-1}\) and 99%. Based on these results, it can be seen that the CTP method results in a higher water flux value than the RTP (Rapid Thermal Process). This is because in the RTP process, the calcination process is not perfect because it is done directly at high temperature. However, the silica membrane with RTP can still be said to have good performance with high salt rejection value so it is still good to use.

Another important view of membrane performance is long-term stability. The longer the membrane shows good performance, the better, stronger and more stable the membrane is. Figure 6 shows the long-term stability silica membrane using wetland saline water taken during rainy season. The performance was performed at room temperature and the pervaporation test was set for over 250 hours.

The results of long term stability indicate that the membrane is stable for the first 100 hours with a water flux of about 1.69 kg m\(^{-2}\) h\(^{-1}\) after which a gradual decay in fluxes had occurred reaching 1.25 kg m\(^{-2}\) h\(^{-1}\) to 250 hours test. Also, the salt rejection remain stable until the desalination reach 100 hours (96.6%) where at the beginning the salt rejection remain 99.01%. The decrease of water flux as well as salt rejection was caused by a blockage by salt molecules on the silica structures as discussed above. This indicates that the membrane matrix may undergo structural changes in the texture and/or buildup of salt molecules that cause clogging of the membrane pores, thus affecting the water flux values.
However, on long-term testing it showed good and better performance, this can be seen that the salt rejection remain above 90% even though the water fluxes decreases

**Figure 5.** Water flux and salt rejection of silica membrane as a function of exposure time over 250 hours in wetland saline water taken during rainy season as a feed at room temperature (26 °C)
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