Desalination Process via Pervaporation of Wetland Saline Water

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Abstract. Water is a very important resource for life on earth. Nowadays, water scarcity is a big issue around the world. Especially people who live in wetland areas, river is an important water source for their daily life. Unfortunately, the water becomes salty due to seawater intrusion into the river. The objective of this work is to apply desalination via pervaporation process of wetland saline water using pure silica membranes employ TEOS (tetraethyl orthosilicate) as a precursor. A two-step acid-base catalysed method has been applied to produce silica sols. The pure silica membranes were calcined under RTP (Rapid Thermal Process) method at 600°C for 1 hour. The various temperatures (20, 40 & 60°C) have been set in pervaporation set up in order to investigate the performance of silica membranes. It was found that at high temperature, silica membranes start to densify and give the lowest rejection compare to lower temperatures (84.9 %). In contrary, there was 100% of water flux increases when the feed temperature increases (from 0.61 to 1.19 kg m⁻² h⁻¹).

Keywords: Desalination via pervaporation, pure silica membranes, sol-gel, dipcoating process, RTP method calcination

1. Introduction

Water scarcity is a big problem nowadays around the world. It was reported that over 2 billion people per day do not have access in clean water[1]. This issue is continuing to increase up to 3.1 billion people by 2050 [2]. If travel to South Kalimantan Indonesia, especially for local people live in wetland areas, the access of clean water also remains similar problem. Most of them are using saline water coming from the river due to the intrusion of sea water. It was reported that river water is salty. This is even worst when it becomes in the dry season, the depth of water reduces and create the salinity of water is higher than rainy season. Beside that, several investigations have reported that those water content organic, iron and manganese contents and give odor with dark brown yellow and low pH (pH 3-4) [3].

Based on these conditions, the application of membrane technology via desalination process is a way to treat saline water to be clean water. Desalination is a process to separate salt molecules in water. There are several types in desalination; membrane distillation (MD), reverse osmosis (RO) and electro dialysis. Unfortunately, those processes are still costly. However, desalination via pervaporation process spend low energy and low cost to apply. Especially when using silica as membrane material. This material is very strong and cheap and good physical and chemical properties [4, 5]. Currently, there are two types of inorganic silica materials widely applied for desalination, such as zeolites and silica. Practically, zeolite membranes have proven to be effective but long-term stability still needs to be improved[6-9]. Silica has excellent molecular sieving properties[10-12] so that it is offering higher selectivity to separate water molecules from the salt molecules. Therefore, we conclude that silica materials provide a good performance as well as hydrothermally stable when applied in membrane technology[13-16]. This study aims investigate the performance of silica membrane using wetland saline water in various temperatures.
2. Methodology

2.1. Silica Sol preparation

20 mL Ethanol was added to a three-neck flask and cooled using to 0°C and stirred using a magnetic stirrer at 250 rpm for 5 minutes. Then 18.66 g TEOS was added into the neck flask three slowly and silenced for 5 minutes while stirring. 8.0699 g HNO₃ 0.00078N was dropped wisely into solution.

The mixtures of Et-Oh + TEOS + HNO₃ were refluxed and stirred for 1 hour at 50°C. After 1 h, the NH₃ solution was added into mixtures and continue refluxed for another 2 hours at the same temperature. At the end, the pH of silica sols was checked.

2.2. Dipcoating and Calcination

Dipcoating process was prepared by immersing the membrane support (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. It then be calcined using RTP (Rapid Thermal Process) method at 600°C for 1 hour. The calcined membranes were cooled at room temperatures. This dipcoating and calcination process were repeated for 4 times.

2.3. Desalination via Pervaporation Process

The first step is to prepare wetland saline water taken during rainy and hot season. Usually the wetland saline water is more salty during hot season compare to rainy season. It is due to the water in the river start to flow into the sea and the salt molecules remain in the river. Reversely, during rainy season more seawater intruded into the river, however, there are a lot more water coming from the rain.

Each of wetland saline water was placed in the feed tank in the pervaporation set up (Figure 1). The silica membranes was connected to the vacuum pump and cold trap and the other side was blocked. This method is called dead end method. The cold trap was condensed in the icebath and the peristaltic pump is applied for controlling the salt concentration in the feed tank (rector). The measurement was taken at various temperature (room temperature/26, 40 and 60 °C). This is aimed to investigate the performance of silica membranes. The pervaporation process was hell for 20 minutes

![Figure 1. Pervaporation set up of wetland saline water as a feed](image)

The next step is to determine the water flux which can be determined by the equation \( F = \frac{m}{(A \Delta t)} \), where \( m \) is the permeate mass (kg) trapped in the cold trap, \( A \) is the active surface area (m²) and \( \Delta t \) is the pervaporation time. To determine the salt rejection, \( R \) (%), the mass of water condensed in the cold trap was measured by conductivity meter. Then calculate the salt concentration from the equation \( R = \frac{(C_f - C_p)}{C_f} \times 100\% \), where \( C_f \) and \( C_p \) are salt concentrations in the feed and permeate (wt. %).
3. Results and Discussion

Sol gel method is the most effective, cheap and simplest way to prepare thin membrane layer. For this work the prepared silica sols at pH=6. This condition has been reported in our work [16] due to the low silanol but high siloxine concentration. This sols likely to form micro and mesoporous structures that is better to separate salt molecules in the feed solution. To be able to investigate those concentrations, the FTIR spectra of calcined silica xerogel was obtained as seen in Figure 2.

![FTIR spectrum](image)

Figure 2. FTIR spectrum

Figure 2 shows several peaks found in the xerogel at the wavelength 1084, 962 and 800 cm\(^{-1}\). Peak at wavelength 1084 and 800 cm\(^{-1}\) are siloxane groups where at 1084 is the vibrational band associated with stretching band of Si-O-Si while at 800 cm\(^{-1}\) is bending vibration of Si-O-Si [17]. Low peak at 962 cm\(^{-1}\) looks like a shoulder attached at wavelength 1084 cm\(^{-1}\) is vibrational of Si-OH (silanol groups). This is also found in our the previous work[16] that an intense peak at wavelength 1070 cm\(^{-1}\) along with lower intensity bands between 1160, 1030 and 800 cm\(^{-1}\) were siloxane groups (Si-O-Si) and another peak at 960 cm\(^{-1}\) which is the group of silanol vibrations (Si-OH).

A part of dried silica xerogel, the solution of silica sols was then is acted as a thin film that is dipcoated onto tubular alumina membrane support (\(\alpha\)-Al\(_2\)O\(_3\) tubular support, pore size \(\approx 100\) nm) via RTP method of calcination at temperature 600 °C for 1 hour hold and without ramping/cooling rates. This dipcoating process was done at a dwell time of 2 min and a dipping and withdrawal rate of 10 and 5 cm min\(^{-1}\), respectively using dipcoater. This entire process produces a layer of pure silica membranes. And, this process was repeated four times in order to get a four layers of silica membranes. The reason is to get a smooth, un-defect and thin membrane layer on top of macroporous alumina membrane support without deposition of interlayer membranes. This membrane was then applied to wetland saline water for desalination held in various temperatures (26, 40 and 60 °C).
Desalination is a process of separation occurred in a phase changing from liquid to vapor on the other side of the membrane. In the desalination process the important thing to know is the value of salt rejection and water flux. Salt rejection shows the ratio of the amount of salt concentration in the feed (salt water) to the permeate of membrane layer. Here is an equation to measure salt rejection:

\[ R = \frac{C_f - C_p}{C_f} \times 100\% \]

(1) Where \( C_f \) and \( C_p \) are the feed and permeate concentrations of salt (wt %).

And the equation to measure water flux is in the following formula:

\[ \text{Flux} = \frac{m}{At} \]

(2) Where \( m \) is mass, \( A \) is the surface area of membrane and \( t \) is time of desalination process held.

The following Figure 2 is the graph of desalination via pervaporation process applied for wetland saline water at temperatures 26, 40 and 60 °C.

The wetland saline water taken during rainy and hot season have different concentration (1.71 and 3.05 wt.%, respectively). The measurement of water fluxes and salt rejections were done for fresh water and both wetland saline water taken during rainy and hot season. It is to investigate the salt concentration of the wetland water as well as the performance of the silica membrane. Also, the measurement was taken placed in room temperature (26), 40 and 60 °C. Similar condition was done for salt rejection measurement. Results show that water fluxes done at room temperature, 40 and 60 °C for fresh water and both wetland saline water taken during rainy and hot season are 0.33–0.61; 0.54–0.76; and 0.84–1.19 kg m\(^{-2}\)h\(^{-1}\), respectively. In addition, the salt rejection for fresh water and both wetland saline water taken during rainy and hot season are 99.95–84.23; 99.95–93.23; and 84.95–69.91 %. From these results, it is clearly shown that the water fluxes increase when the temperature increase. In the contrary, the salt rejection decrease when the temperatures increase.

Remarkably, the water fluxes reported were quite low, however, the salt rejection show good stability and effectively produce potable water exclude at high temperature (>60 °C).

The following results of water fluxes and salt rejections can be seen in Figure 3 below:

**Figure 3.** Performance of pure silica membranes for wetland saline water rainy and hot season, (i) bar charts are water fluxes (left axis), and (ii) line scatters are salt rejections (right axis)
It can be seen at Figure 3, at the measurement at 60°C, the salt rejection was dropped dramatically 69.91%. It seems the membrane pores cannot survive operated at high temperature. It is due to the damaged pore structure. Similarly to our previous work[16], the membrane performance was decreased when membrane was exposure at temperature 75°C due to the reduction of pore structure significantly.

Figure 3 shows the image of pure tubular silica membrane. From this figure can be seen that the membrane produces is shiny and smooth. The color of membrane layer is transparent so that the white color is coming from the alumina tubular membrane support itself.

![Figure 3. Image of pure tubular silica membrane.](image)

In conclusion, the performance of pure silica membrane was very stable at room temperature to 40 degree. And, this membrane process was not recommended to be applied at high temperature (up to 60°C). It is due to at high temperature, it is easily densified and surface (the pores) of membrane was cracked and easily damaged. However, the overall performances, this membrane show good performance to be applied for treating wetland saline water.

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5. References

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