

Silica P123 Membranes for Desalination of Wetland Saline Water in South Kalimantan

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Abstract. Salt water intrusion into the river around wetland areas is affected by the increasing of sea water level. This work aims to fabricate silica P123 membranes applied for desalination of wetland saline water. This type of membranes is produced by combining silica material (TEOS) with P123 as organic polymer. The calcination method was varied from 350°C and 600°C for an hour using RTP method. The desalination via pervaporation process was applied in order to investigate water flux and salt rejection. The results show that membranes calcined at low temperatures obtain good performance compare to high temperature (4.105 and 3.904 kg.m⁻².h⁻¹ for water flux and 96.22 and 65.67% for salt rejection obtained from membranes calcined at 350 and 600°C, respectively).

Keywords: Desalination via pervaporation, silica P123 membranes, salt rejection, water flux

1. Introduction

Water is the most essential substances on earth. There was no life if there is no water. Nowadays, water scarcity become big issue around the world as well as in Indonesia. It is due to rapid population growth, climate change, and water and waste management are not appropriate. This problem is a great challenge for the continuity and availability of clean water in South Kalimantan especially in the communities of wetland areas.

People get used to use water from rivers for their daily live whereas those rivers are usually salty due to seawater intrusion. UNICEF reported that Indonesia currently not on track to achieve safe water and estimates that as many as 1,400 children under five die every day from diarrheal diseases are closely related to the lack of clean water and adequate sanitation and hygiene. In fact, every year, Indonesia suffered a loss of \$ 6.3 billion due to poor sanitation. By improving sanitation, Indonesia has the potential to contribute as much as \$ 4.5 billion for economic growth. This is because the reduction of water resource and availability of clean water. Desalination process is an alternative key to overcome this problem, i.e. conventional distillation, reverse osmosis, electro dialysis and membrane distillation.

This process usually applied in membrane technology. It has been reported that this technology has been widely used in separation processes due to faster processes, more efficient and no phase changes in separated solutions. It is also known as a cheap method in its application. Zeolite and silica are inorganic materials which are mostly used in membrane technology for desalination processes. Silica materials especially combined with organic templates as well as surfactants have been reported as good hydrostability and molecular sieving membranes in desalination.

This work aims to fabricate Silica P123 membranes with dipcoated with multiple layers (4 layers) and calcined with different temperature (350 & 600 °C) for 1 hour using RTP (Rapid Thermal Processing) method. The performance of membranes was measurement using wetland saline water from the salty river in South Kalimantan.



2. Methodology

2.1 Silica P123 Sol Gel Synthesis and Xerogel Characterisation

Silica P123 sols was synthesized by combining silica sols with polymer 35 wt % P123 (Pluronic 123) (Sigma Aldrich). Silica sols were made using precursor TEOS(tetraethyl or thosilicate), 0.00078 N HNO₃, 0.0003N NH₃, H₂O and Ethanol with 1:0.0007:0.003:5:38 molar ratios. First of all, 20 ml EtOH was added wisely into bottle sample then added 18.66 grams TEOS also dropped wisely. the mixtures of solution werestirred for 5 minutes at 0°C in ice-bath. 8,0699 grams HNO₃ 0,00078N was dropped wisely into the mixtures, and the mixtures were refluxed for an hour at 50°C.

Then 141.127 mL NH₃ 0,0003N was added into solution drop wisely during reflux, mixtures were then continued toreflux for another 2 hours at 50 °C, sols mixtures were then cooled at room temperature with pHchecked. 0.6388 grams P123 (Sigma Aldrich) was added into 50 mL silica sols and stirred at 60 rpm for 45 min. The mixture of Silica and P123 were then dried at 60°C in the oven for 24 h to obtain the dried gel which was grounded into powder and calcined at 350°C and 600°C separately. Silica P123 xerogels was characterized by Fourier Transform Infrared (FTIR) in order to investigate the functional groups of each components.

2.2 Silica P123 Membranes Fabrication

The macroporous alumina substrates (α -Al₂O₃ tubular support ($\phi = 100$ nm) was dipcoated with Silica P123 Sols solutions shown in **Figure 1** and then was calcined at 350°C and 600°C separately for an hour and let it cooled at room temperature. This process was repeated four times to get 4 layers of silica P123 membranes dipcoated onto macroporous tubular membranes support.

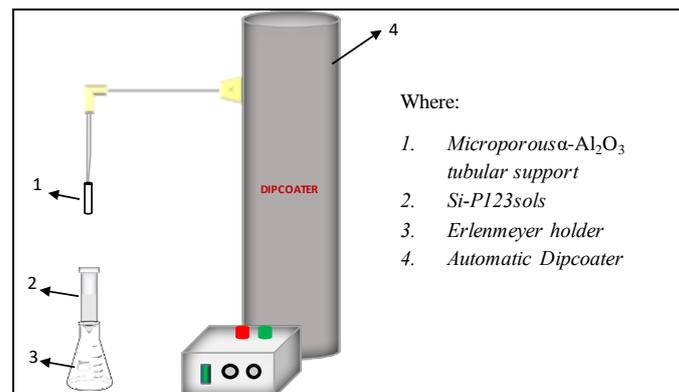


Figure 1.Dipcoating Apparatus

2.3 Desalination via Pervaporation Process

Pervaporation set-up assembled as shown in **Figure 2**. The Silica P123 membrane was blocked at one end and connected to a cold trap and vacuum pump at the other end. The membrane was immersed in a tank containing wetland saline water. Pervaporation was held for 20 min with four times repetitions. The water flux F ($\text{kg m}^{-2} \text{h}^{-1}$), was determined based on the equation $F=m/(A \times \Delta t)$, where m is the mass of permeate (kg) retained in the cold trap, A is the surface-active area (m^2) of the membrane and Δt is the time measurement (h).

The salt rejection, R (%), was calculated as $R=(C_f-C_p)/C_f \times 100\%$, where C_f and C_p are the feed and permeate concentrations of salt (wt%)[15]. The salt concentrations were correlated to conductivities of the retentate and permeate solutions determined by a conductivity meter.

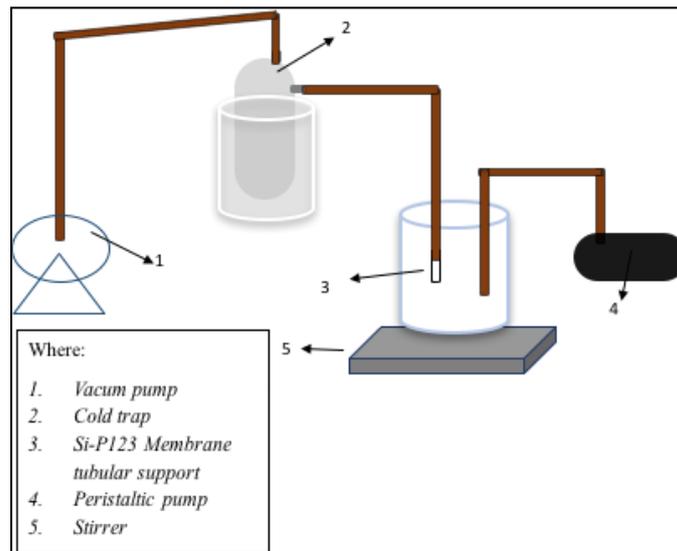


Figure 2. Pervaporation Apparatus

3. Results and Discussions

In preparation of Silica P123 membranes by sol gel method obtained silica sols pH 6. Based on our previous works [9, 12-14] this kind of sols produces mesoporous structure where it is very suitable to separate salt molecules and allow water molecules pass through the membrane matrices [9]. This silica sol was transparent and colorless solution, however after added by P123, the viscosity was a little bit increased. In addition to providing strength to the membrane pores, the addition of P123 in silica sol will affect the silanol and siloxane groups in the silica structures. Silanol and siloxane groups are known to affect pore size of the membrane [15]. The FTIR spectra of calcined silica P123 xerogel (350 and 600°C) is clearly shown in the following graphic.

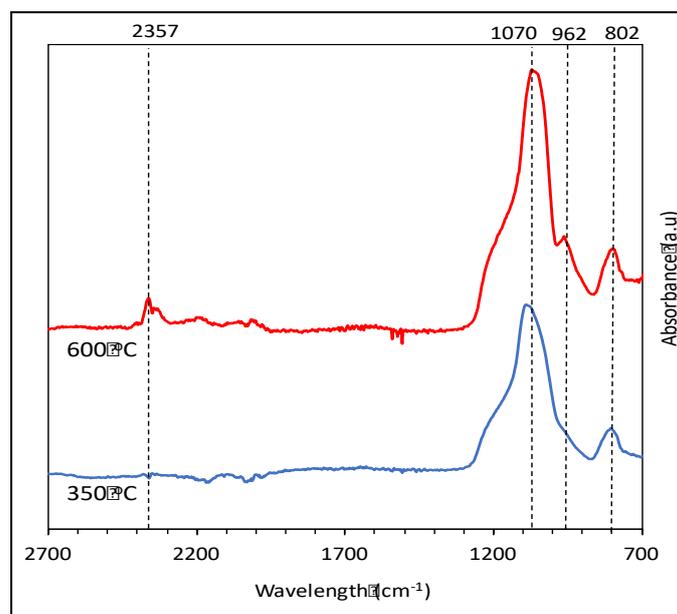


Figure 3. FTIR Spectra of Si-P123 calcined xerogels

Figure 3 shows the FTIR spectra for silica P123 xerogel calcined at 350°C and 600°C in air using RTP method of calcination held for 1 hour. At wavelength 802 cm⁻¹, it was found that there was symmetric stretching of Si-O-Si groups in the spectra at wavelength 802 cm⁻¹. In addition to wavelength 1070 cm⁻¹, there was asymmetric stretching of Si-O-Si groups. Xerogels calcined between 350 and 600 °C under RTP method show similar peaks.

However, the concentration of siloxane group for xerogels calcined at 600 °C is a bit higher. It is due to the temperature of calcination creates more condensation reaction to produce siloxane groups in the matrices. Moreover, at the wavelength 962 cm⁻¹, the IR spectra shows the vibration mode between Si-OH where at this band the formation of silanol group is much higher for xerogels calcined at 600 °C compare to 350 °C. At band 2357 cm⁻¹, there is vibration of Si-C. Xerogel calcined at 600 °C shows a peak of Si-C whereas at 350 °C there is no peak found. It is interesting result saying that at higher temperatures, the composition of carbon clearly shown (maybe it has decomposition to be carbon) and creates pore structures become bigger and wider.

Water flux calculation is used to express the degree to which water through the membrane. The flux value of the membrane is directly proportional to temperature and pressure [16]. Flux calculated with this equation:

$$\text{Flux} = \frac{m}{A \cdot t}$$

where m is the mass of permeate (kg) retained in the cold trap, A is the surface-active area (m²) of the membrane and Δt is the time measurement (h). Salt rejection as a percentage of contaminants removed from the feed stream to the membrane. The equation used to get a percentage of salt rejection was:

$$R = \frac{c_f - c_p}{c_f} \times 100\%$$

where C_f and C_p are the feed and permeate concentrations of salt (wt%). The salt concentrations were correlated to conductivities of the retentate and permeate solutions determined by a conductivity metre.

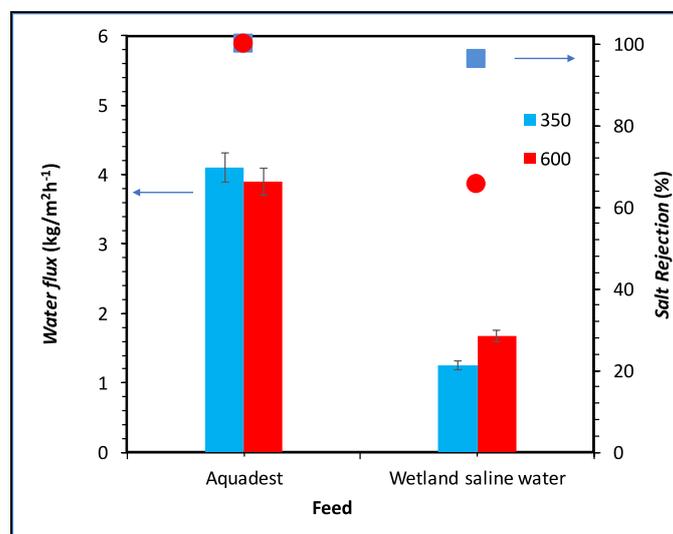


Figure 4. Performance of Silica P123 Membranes using aquadest and wetland saline water as feed versus calcination temperature 300 & 600 °C

Figure 5 shows the performance of Silica P123 membranes (water flux and salt rejection) for membranes calcined at 350°C and 600°C in air. The water fluxes using fresh water (aquadest) show the higher fluxes for both membranes calcined at 350°C and 600°C in air; 4.1 & 3.9 kg m⁻² h⁻¹. In the contrary, when the wetland saline water were used as a feed, the water fluxes and salt rejection decrease sharply (1.25 & 1.67 kg m⁻² h⁻¹ and 96.22 & 65.67 %, respectively). This is clearly explained that the silica P123 membranes calcined at lower temperatures show better performance even though the water flux is a bit lower than the silica P123 membranes calcined at higher temperature. It is also explained at Figure 3 that the functional groups of silanols as well as siloxane groups, for xerogels calcined at 600 °C show higher concentration than xerogels calcined at 350 °C. In addition, when xerogels calcined at high temperature (600 °C), the Si-C bridges will be decomposed (see Figure 3). So that, the silica structures give higher pores and higher silanols that is easily densified. That is why the salt rejection for silica P123 membranes calcined at 600 °C show low rejection (unstable hydrostability). This work does not match with the prior work [8], it is due to the calcination method used (CTP=conventional thermal processing versus RTP methods). It can be concluded that the carbon templated on the silica surface affect a better performance of the membrane in terms of water flux and salt rejection.

5. Acknowledgment

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