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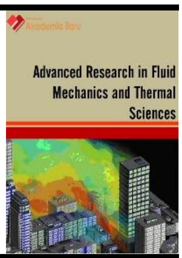

Rapid Thermal Processing and Long Term Stability of Interlayer-free Silica-P123 Membranes for Wetland Saline Water Desalination

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ABSTRACT

The intrusion of sea water through to wetland areas creates wetland water became saline and very poor quality of water. For that, the interlayer-free silica-P123 (Si-P123) membranes calcined via rapid thermal processing (RTP) method was successfully investigated for desalination of wetland saline water. RTP method is a fast and low costs method to fabricate Si-P123 membranes compare to conventional thermal processing (CTP) method. The aims of this works are to improve the stability of silica base membranes by templating triblock copolymer P123 as carbon sources into silica matrices, and also to investigate the performance and long-term stability of Si-P123 membranes calcined under RTP method. Desalination through pervaporation process have been applied to produce potable water. Results shows the highest water flux of Si-P123 membrane calcined at 350 °C was 2.6 - 4.5 kg m-2 h-1. It was also found that this membrane was offering high surface area of 572 m2 g-1 and give mesopore structures (2.2 nm). For that, the performance of salt rejection was excellent (>98%). Furthermore, long-term stability appeared very stable for water fluxes and salt rejections measurement (over 400 h). Moreover, the permeate salt concentration was excellent (99% still under WHO limit standard (600 ppm) of potable water. It can be concluded that the stability of Si-P123 membrane was very robust for wetland saline water desalination for over 400 h of long-term stability.

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1. Introduction

Water crisis is critical issue occurring in wetland area, especially in South Kalimantan, Indonesia. Due to that the societies were force using wetland water to meet household water needed. Wetland area is commonly found in a tropical ecosystem and its water have poor qualities due to containing high amount of natural organic matter (NOM) which does not meet World Health Organization (WHO) standard. Moreover, sea water intrusion occurs during hot season and bring out increasing salt concentration called wetland saline water. Desalination is necessary as alternative technology for providing the fresh water [1].

In recent years, membrane processes have been considered for desalination [2]. Moreover, NOMs in wetland water is a major pollutant in surface water [3]. Previous study was reporting the membrane technology was capable for treating wetland water via ultrafiltration (UF) by polysulfone membrane [4]. However, membrane technology has a limitation for treating water with high NOM content. Yunos *et al.,* [5] was found NOM have contributed to fouling on polysulfone membrane and lead the water flux decrease drastically on UF process for treating surface water. Pervaporation is a desalination technology which promise to produce fresh water with low energy consumption (based on low pressure) and give high water flux better than reverse osmosis [6-7].

Commonly inorganic membrane (i.e. alumina, zeolite and silica) more widely used for pervaporation. Silica membrane was offering high molecular sieving compared zeolite and organic materials [8], thermal resistance, robustness and handy for desalination process [2]. Silica membranes were simple synthesis via sol-gel method [9]. Silanol (Si-OH) group was formed via sol-gel process by employing acid catalyst at partial hydrolysis reaction and produce microporous silica thin film with pore sizes less than 1 nm [10]. Silanol has hydrophilic properties that brings silica matrices collapse when is contact to H_2O molecules and led salt rejection drop drastically [2]. In order hand to improving hydro-stability of silica membrane, previous studies have been conducted by carbonized template to silica matrices [11-12]. Carbon template is assisting silica membrane become hydrophobic and provides a hindrance for the diffusion of unstable silanol group. Recent advances have shown that these carbon template silica membranes can be synthesis without intermediate layer. Instead of conventional silica membranes with interlayers, thus reducing the cost of silica membrane fabrication [13]. Other than that, silica membrane preparation method is usually done via conventional thermal processing (CTP) method similar to Elma *et al.,* [14]. Generally, CTP method spent 2 days/layer for drying, heating and cooling rates, and calcination, so that implies to costly [15]. The innovative concept was demonstration by rapid thermal processing (RTP) method for preparation silica membrane to speed up overall time processing [16-17]. It takes less than 1 day to fabrication of silica membrane compare to CTP [16]. Hence, in this work we selected interlayer-free carbon template silica membranes (Si-P123) by RTP method and investigate their performance for desalination of wetland saline water.

2. Methodology

2.1 Chemical and Material

Wetland saline water was collected from Muara Halayung village, South Kalimantan, Indonesia. during hot season (3.2 wt% NaCl). Silica sol was conducted by a two-step acid-base sol gel method using tetraethyl orthosilicate (TEOS, 99,0%, Sigma-Aldrich) as precursor of silicate and triblock copolymer Pluronic P123 (PEG, 35 wt%, Sigma-Aldrich) as carbon template. Ethanol (EtOH, 99.0%) and aquadest as solvent and dilute nitric acid (0.0008 M HNO3, Merck) and ammonia (0.0003 M NH3, Merck) as acid-base catalysts.

2.2 *Fabrication and Characterization of P123 Membrane*

In this work, RTP method is required to use for preparation of silica-P123 membrane. Silica sol synthesis procedure was detail described on previous work [18]. Finally, Si-P123 (Silica-P123) sol was conducted with final molar ratios is the TEOS:EtOH:HNO_3:H_2O:NH_3:P123 sol were calculated to be 1:38:0.0008:5:0.0003:0.00024.

Si-P123 membrane was prepared by dip-coated of macroporous alumina substrates α-Al_2O_3 tubular support (Ceramic Oxide Fabricators, Australia) with average pore size is 100 nm into Si-P123 sol four times to produced 4 layers. Every membrane layer was calcined based on treatment described above for xerogel synthesis after deposition of coating membrane. The membranes thickness and morphology were examined using scanning electron microscopy (SEM ZEISS).

2.3 Membranes Performance Experiment

Long terms and performance of Si-P123 membrane was determined by pervaporation experiment for wetland saline water desalination. Feed solution was prepared with sodium chloride (NaCl, Sigma-Aldrich) dissolved in aquadest with salt concentration range 0.3-5 wt% and temperature was varied at ~25 °C (room temperature), 40 °C and 60 °C which was controlled via hotplate and thermometer. Wetland saline water was treated similar as salt concentration feed treatment. Membrane was submerged into feed water (wetland saline water and varied salt concentration). To avoid concentration polarization on membrane surface, the feed solution was recirculated by peristaltic pump. The salt concentrations were correlated to retentate and permeate solutions conductivities was determined by a conductivity meter (OHAUS).

3. Results
3.1 Membrane Morphology

Morphology structure of Si-P123 membrane was analysis by SEM on Figure 1. This membrane is thicker than membrane fabricated by Elma *et al.,* [19]. In this work, thickness of Si-P123 thin film is approximately ~1 µm (Figure 1). Commonly, inorganic membrane derived silica material has thickness range 30-50 nm of thin film if calcined by CTP [2]. Therefore, RTP method is produced >50 nm of thin film thickness. In this membrane, infiltration effect is clearly observed. The membrane morphology showing the cracking surface on top layer and significantly have the roughness and boulders of the alumina particle protruding on Si-P123 membrane surface. This result displayed RTP at air calcination lead to wide spread of cracks in the carbonized templated silica top film similar to Elma *et al.,* [19] work with N_2 calcination. Other than that, the surface area of Si-P123 membrane shows not delicate. It was causing by this membrane was not used interlayer or called interlayer-free like our previous work [19-21].

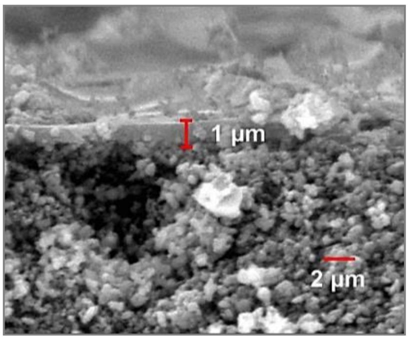

Fig. 1. SEM image of silica-p123 membrane calcined at 350 °C via RTP (cross section perspective)

3.2 Membrane Performance

Interlayer-free membranes with four layers were prepared by RTP method and two acid-based catalyst with varied calcine temperature (300 °C, 350 °C and 450 °C) in air furnace. For completeness these membranes were tested for desalination via pervaporation process. Figure 2 shows the result of membrane performance in terms of water permeate fluxes and salt rejections in various salt feed concentration (NaCl 0-5 wt%) and application for wetland saline water (NaCl 3.2 wt%). The water fluxes were decreased by increasing feed salt concentration (Figure 2). It is due to concentration polarization of salt on feed solution which led the water flux decrease.

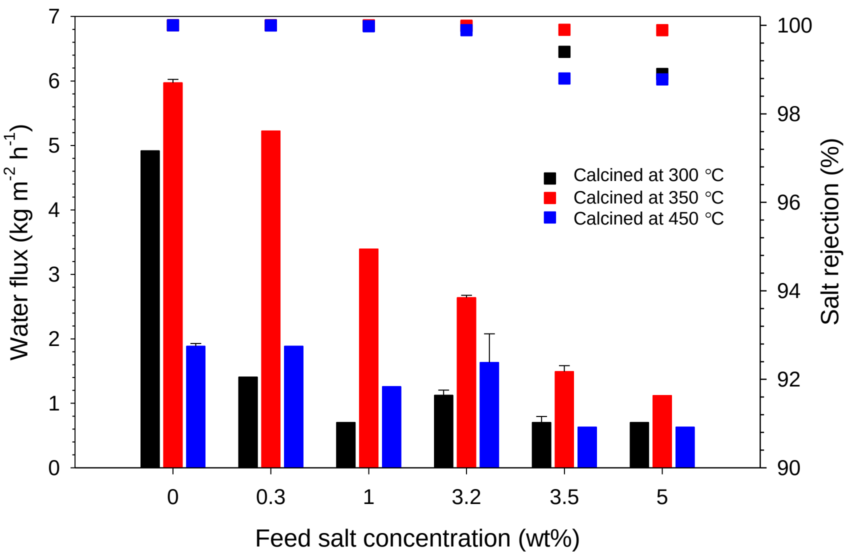

Fig. 2. Performance of Si-P123 membranes varied RTP temperature for water flux and salt rejection

An interestingly, the result was obtained excellent water flux was performed on Si-P123 membrane calcined at 350 °C is 60% higher than membrane calcined at 450 °C. Calcine temperature is very influence toward resulted of silica thin film structure. This result shows the water flux of Elma *et al.,* [19] work is slightly higher than silica-P123 membrane in this work. It caused by this membrane was calcined via RTP method on air condition. Furthermore, Elma *et al.,* [19] have done it by CTP method under vacuum. Nevertheless, this membrane is much low costly to fabricate instead using CTP. In consequence of silica membrane by RTP method was extremely brief to produce [22]. In high calcine temperature, carbon template become disappear owing to decomposition organic material. Pure silica membrane (without P123 carbonized template) was approve unstable for desalination, so that membrane performance was delivered poor salt rejection [11,19,21,23]. Hence salt rejection of Silica-P123 membrane resulted excellent take over ~99% for all multiple calcined membrane (Figure 2).

Performance of SI-P123 membrane calcined at 350 °C was shows on Figure 3, water flux by function of feed salt concentration (0-5% wt NaCl) was measured at temperature 25, 40 and 60 °C. Water flux of membrane Si-P123 calcined at 350 °C by RTP method was increased by increasing of feed temperature. It is necessary that high water flux reach value of 4.4 kg m^{-2} h^{-1} (wetland saline water, 3.2% wt NaCl) and 3.8 kg m^{-2} h^{-1} (sea water, 3.5% wt NaCl) at 60 °C. In addition, salt rejection was worthy good over 98% in all feed salt concentration. It is clearly proof that employed P123 carbonised into silica membrane was state of the art.

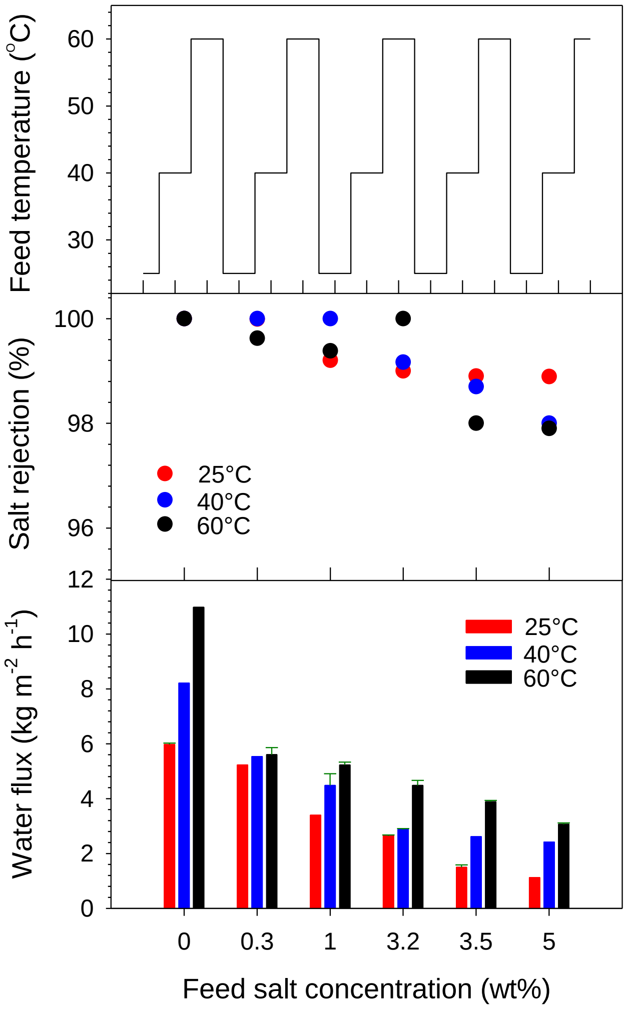

Fig. 3. Membrane performance at varied salt concentration and feed temperature (25, 40 and 60 °C)

Table 1 shows summary of multiple silica membrane type performance for desalination. The highest membrane performance through water flux measurement shown for work done by Elma *et al.,* [20] using cobalt as template agent to silica matrices. However, cobalt is not necessary used for treating water due to may polluted and harm water to consumption. When compared to hybrid organo silica membrane performance also shows high water flux of 2 to 20 kg m^{-2} h^{-1} Elma *et al.,* [21].

It possibly caused effect of hybrid membrane coupled with carbon hydrophobicity and high temperature and led vapor pressure diffused fast through the membrane derived from TEVS. Si-P123 membrane in this work was show better performance offered 37.5% higher of water flux. It is suggested to triblock copolymer material served amount of carbon chains P123 promoted silica matrices to be stronger. In other hand silica membrane without carbon template performed high water fluxes but its long term stability was not worthy for desalination [24]. Moreover, water flux of Si-P123 membranes in our work resulted good with high water flux if compare to other carbon silica template membrane [16,19].

Table 1
Performance of multiple silica membrane type for desalination

Membrane type	Calcination method	Feed temp. (°C)	Feed concentration (%)	Water flux (kg.m^{-2}.h^{-1})	Salt rejection (%)	Ref.
Si-P123 calcined at 350 °C	RTP (air)	25-60	0.3-5	1.1-5.6	99.2	This work
Silica membrane	RTP (air)	26	0.3-15	1.2-2.9	>95	[24]
Hybrid membrane	CTP (vacuum)	25-60	1-15	2.3-5.7	>99.7	[16]
Carbonised P123-35 silica template	CTP (vacuum)	22-60	0.3-7.5	1.7-8.4	>99.5	[19]
Carbonised C16 silica template	CTP (vacuum)	60	0.3-3.5	2.1-3.1	91-97%	[11]
Hybrid TEVS-P123	CTP (vacuum)	60	0.3	3.7	>95	[25]
Hybrid organo-silica	CTP (air)	22-60	0.3-7.5	2-21	>98	[21]
Silica-cobalt-20	CTP (vacuum)	22-60	0.3-7.5	0.6-25.8	>90	[20]

As shown in Figure 4 further stability testing hydro-stability of Si-P123 membrane for wetland saline water desalination at room temperature (25 °C) were carried out for 480 h. There is small marginal fluctuation of water fluxes averaging at 2.6 kg m^{-2} h^{-1} and fluctuation of high salt rejection over 99% for Si-P123 membrane performance (Figure 4(a)). The result of long terms stability of Si-P123 at 350 °C membrane matrices may be structural changes by salt residues causing pore blocking [14]. The water flux was decreasing sharply after 1 hour operation, it shows different result compared to Elma *et al.,* [14] work, due to using differences of membrane and feed solution with this work. It is due to wetland saline water has unique characteristic containing numbered of natural organic matter (NOM) [26]. NOM was contributed to decreasing water flux of membrane. So that water flux of membrane used in this work got the effect from NOM as the rejection also gradually decreased. Even though, function of water flux was decreased by the time, permeate salt concentration all the time still comply and meet WHO salt limits standard for drinking water (Figure 4(b)).

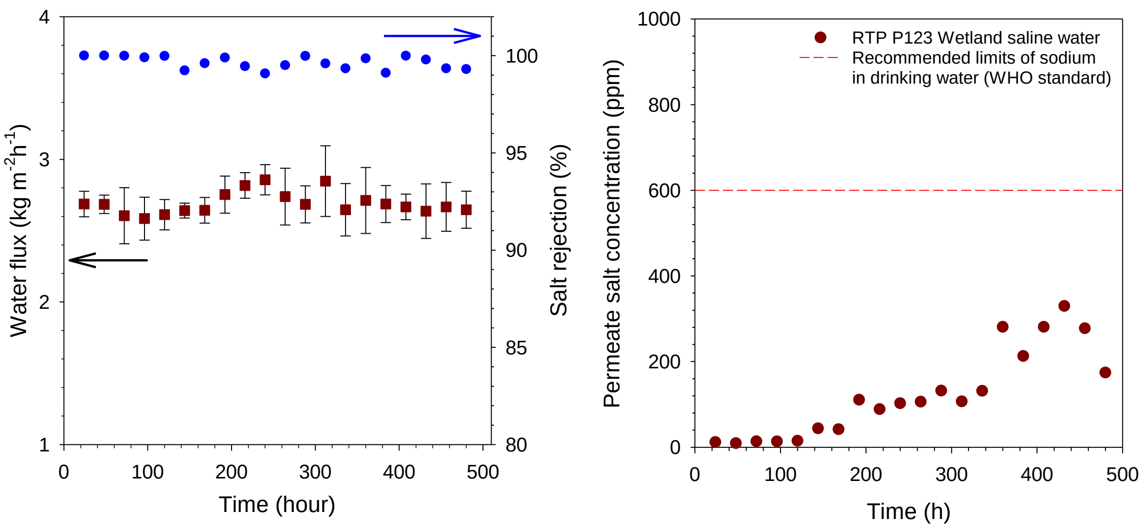

Fig. 4. (a) Long term performance of Si-P123 RTP membrane for wetland saline water desalination, (b) permeate salt concentration

4. Conclusions

Interlayer-free Silika-P123 membrane was successfully fabricated using sol gel method, dip-coating and calcination process via RTP. TEOS employed as silica precursor. These membranes were templated using P123 into silica matrices and calcined at 300 °C, 350 °C and 450 °C in air condition. As fabricated the membranes demonstrated excellent desalination of wetland saline water (3.2 wt% NaCl) via pervaporation, achieving a best result of higher water flux shown on Si-P123 calcined at 350 °C (2.6-4.5 kg.m^{-2}h^{-1}) at feed temperature 60 °C. Moreover, salt rejection performed excellent over 98% for all membrane testing and compare to previous work. It concluded that Si-P123 membrane is promising due to robust and suitable for water desalination.

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