

# Organosilica Multichannel Membranes Prepared by Inner Coating Method Applied for Brackish Water Desalination

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## Organosilica Multichannel Membranes Prepared by Inner Coating Method Applied for Brackish Water Desalination

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**Abstract.** A sol-gel method has been widely utilized for membrane fabrication due to low temperatures requirement and high purity. In the application of potable water production, membrane technology also plays an important role applied for brackish water treatment. This study aims to develop a multichannel membrane through an inner coating method and then to demonstrate the membrane performance for brackish water desalination. Two types of organosilica multichannel membranes were fabricated by mixing TEOS as a silica precursor using citric acid catalyst via sol-gel method and pectin as carbon templated. The multichannel membranes were inner-coated up 4 layers and calcined at 175 °C for organosilica multichannel membrane and 300 °C for silica-pectin multichannel membranes in vacuum condition. From FTIR results indicated that organosilica and silica-pectin multichannel membranes show siloxane (Si-O-Si), silanol (Si-OH) and silica-carbon (Si-C) groups. In addition, the organosilica multichannel membrane performed the water flux of 15.74 kg.m<sup>-2</sup>.h<sup>-1</sup> and salt rejection of 99.77%, where the silica pectin multichannel membrane performed the lower performance compare to organosilica multichannel membrane (water flux: 11.44 kg.m<sup>-2</sup>.h<sup>-1</sup> and salt rejection: 99.48%). In conclusion, the organosilica multichannel membrane derived from citric acid as catalyst has a better performance compare to organosilica multichannel membrane derived from pectin applied for brackish water treatment.

### Introduction

Currently, a clean water availability has been concerned in developing countries. The problem encourage the use of membrane technology as an alternative to process salt water into drinking water by desalination process [1, 2] as well as organic rejection [3-7]. The advantages of membranes include energy saving, clean, relatively free of waste and ability to separate temperature sensitive solutions [8-13].

In terms of material, organo silica membranes are widely used for desalination which are made of silica and carbon. Carbon has been inserte to increase the strength of the silica membrane [14-16]. In addition, organo silica membranes made with the addition of citric acid can also be utilized to produce carbon groups to strengthen the matrix structure on thin-films as in the study [17, 18]. Elma, et al. was introducing pure silica membrane for water desalination by rapid thermal process, which only need a day to produced silica thin film for four layers [19, 20]. Another study used pectin, citric acid and triblock copolymer P123 as a carbon source which was inserted into a silica matrix to increase hydrostability [21-24]. A study done by Assyaifi, et al. [25] also reported that carbon from pectin could increase silica membrane performance applied for photocatalytic-pervaporation of wetland saline water.

Multichannel membranes have many holes which can increase the surface area of the membrane, resulting in higher flux than membranes with one hole [26]. The tubular multichannel also has a pore size between 8-10 nm, porosity ranging from 30-35% and mechanical strength between 5000-6000 MPa [26]. The direct deposition of alumina particles onto the inner wall of a porous alumina tube was successfully made from a nano-sub micro bimodal suspension by EPD. A higher thickness of deposits invariably exhibited cracks and delamination from the substrate surface [27]. The substrate/deposit interaction in the MCVD method, MCVD method combined with the solution doping and sol-gel method has been experimentally proved. This interaction increases the diameter of the core of a preform obtained by the collapse of the substrate tube coated on the inner wall by a thin layer. Moreover, the interaction decreases the dopant concentration in the core and consequently the refractive index. In the case of hardly sinterable dopants (rare-earth oxides,  $\text{Al}_2\text{O}_3$ ) it may increase the attenuation of the prepared fibers [28].

Elma, et al. has reported that vacuum calcination resulted in a more mesoporous silica matrix and higher carbon yield compared to  $\text{N}_2$  calcination, resulting in relatively superior performance during the desalination process [29]. This study aims to develop a multichannel membrane through an inner coating method and then to demonstrate the membrane performance for brackish water desalination (NaCl 0.3%) as feed. The tubular multichannel membrane will be inner coated with an organo silica thin film only on the inner side through the inner coating method. In this study, there are 2 types of silica membranes that take carbon sources from citric acid and pectin.

### Methodology

**Xerogel synthesis and characterisation.** Silica sol is prepared by mixing 18.66 gram TEOS as silica precursor into 20 mL ethanol at  $0^\circ\text{C}$ . Then added catalyst 8.07 g of dilute citric acid (0.00078 M) for organo silica 8.07 g of dilute nitric acid and refluxed for 1 hour at  $50^\circ\text{C}$ . Next, 142 mL ammonia was added, which was refluxed for 2 hours under the same conditions. After cooling, measure the pH of the silica sol. Pectin concentration (%w/v) 0.5% was dissolved into the previously prepared sol for 45 minutes at  $0^\circ\text{C}$  for silica pectin. Xerogel was made by drying silica-pectin sol in an oven at  $60^\circ\text{C}$  for 24 hours and then grinding the xerogel. Then the xerogel was calcined for further characterization using Fourier Transform Infra-Red (FT-IR) and deconvolution was calculated using fitlyk software.

**Membrane preparation.** The multichannel membrane inner coating process is carried out using an inner coater. Membrane coating is done by coating the inside of a multichannel membrane into a sol gel that has been made with a flow rate in the membrane for 2 minutes. Calcination under vacuum conditions was carried out for 1 hour with a temperature variation of  $175^\circ\text{C}$  for organo silica and  $300^\circ\text{C}$  for silica pectin. After calcining, cooled for 30 minutes. This process is repeated up to 4 times to obtain 4 layers. Inner coater module can be seen in Fig. 1 below.

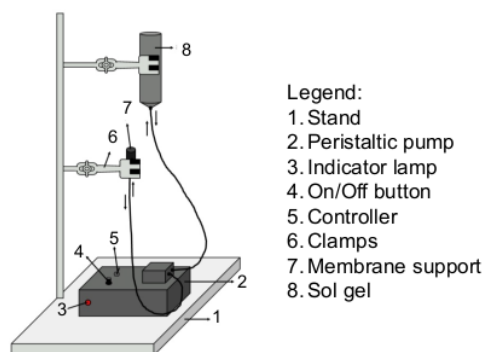


Figure 1. Inner Coater Module

The organo-silica and silica pectin inner coating membrane was then applied to NaCl 0.3% using a pervaporation system. The working principle of the pervaporation system is that in the presence of a temperature difference as a driving force, the air feeds through the membrane and changes the phase into steam (steam). The steam produced will be accommodated in a cold trap and condensed to obtain air processing (permeate). Performance is determined by calculating the flux and salt rejection. The water flux,  $F$  ( $\text{kg m}^{-2} \text{h}^{-1}$ ) and salt rejection,  $R$  (%) can be calculated using the equation below:

$$F = \frac{m}{A\Delta t} \quad (1)$$

$$R = \frac{(C_f - C_p)}{C_f \times 100\%} \quad (2)$$

Water flux calculated using equation (1), where  $m$  is the permeate mass (kg) in the cold trap,  $A$  is the membrane surface area ( $\text{m}^2$ ) and  $\Delta t$  is the time operation (hour). Salt rejection,  $R$  (%), obtained based on equation (2), where  $C_f$  and  $C_p$  are the feed and permeate salt concentrations (wt%). The salt concentrations were correlated to conductivities of the retentate and permeate solutions tested by a conductivity meter.

### Result and Discussions

The sol gel method is a method that is often used in the manufacture of thin films [30]. The sol-gel method has several advantages, including: the process takes place at low temperatures, the process is relatively easy, can be applied in all conditions, produces products with high purity and high homogeneity. If the parameters are varied, the pore size and distribution can be controlled. In addition, the sol-gel process is relatively inexpensive and the product is a non-toxic silica xerogel [31]. In sol-gel synthesis, hydrolysis and condensation reactions are involved. The hydrolysis reaction occurs during the process of dissolving the precursor into alcohol, water and the addition of a catalyst [32]. Colloidal sol is produced from the hydrolysis reaction. After hydrolysis, it is followed by a condensation reaction which will form a gel [30].

In the hydrolysis reaction, the alkoxide group (OR, where R is the alkyl group,  $\text{C}_x\text{H}_{2x+1}$ ) is replaced by a hydroxyl group (OH). The silanol group (Si-OH) is then involved in the reaction producing condensation bonds of siloxane (Si-O-Si), alcohol (R-OH) and water [33]. Pore formation can be controlled through a sol-gel process with the addition of a catalyst. The addition of acid catalysts (such as HCl,  $\text{HNO}_3$ ,  $\text{CH}_3\text{COOH}$ ) will increase the formation of Si-OH bonds (silanol groups) which makes the pore size tend to be micro (<2 nm) [34]. Meanwhile, using an alkaline catalyst (such as  $\text{NH}_3$ ) can increase the number of siloxane groups, namely Si-O-Si bridges (siloxane bridges).

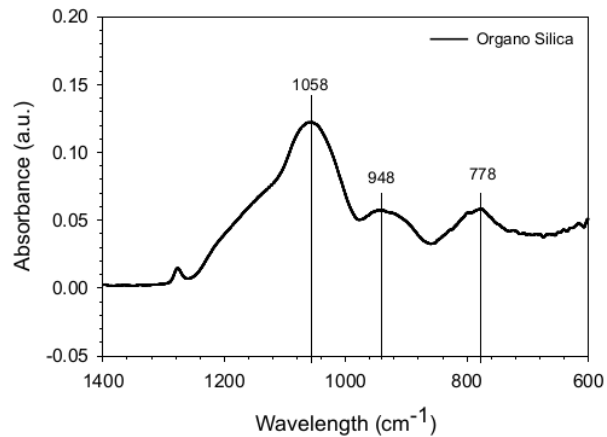


Figure 2. Spectrum FTIR Xerogel Organo Silica

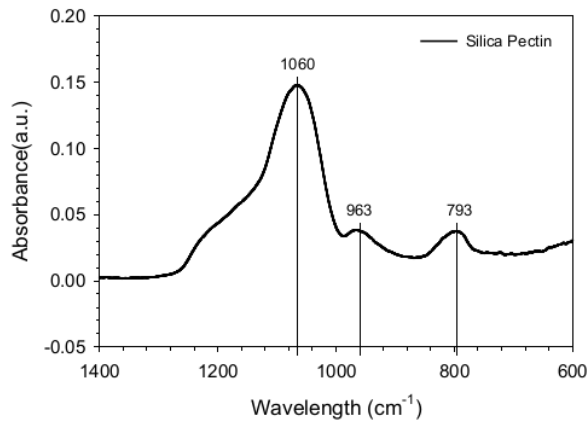


Figure 3. Spectrum FTIR Xerogel Silica Pectin

It can be seen that the FTIR spectrum of organo silica xerogel and silica pectin xerogel has siloxane (Si-O-Si) group and silanol (Si-OH) group as shown on Fig. 2 and Fig. 3. Siloxane group for organo silica is seen at wavelength of  $1058 \text{ cm}^{-1}$  while the silanol group is seen at a wavelength of  $948 \text{ cm}^{-1}$  and silica carbon at a wavelength of  $778 \text{ cm}^{-1}$ . Siloxane group for silica pectin is seen at wavelength of  $1061 \text{ cm}^{-1}$  while the silanol group is seen at a wavelength of  $970 \text{ cm}^{-1}$  and silica carbon at a wavelength of  $793 \text{ cm}^{-1}$ . This is in accordance with the theory, according to [35] the peak wavelengths of siloxane (Si-O-Si) and silanol (Si-OH) are  $1060 \text{ cm}^{-1}$  and  $980 \text{ cm}^{-1}$ , silica carbon groups (Si-C) is found at a wavelength of  $800 \text{ cm}^{-1}$ . In addition, the multiple peaks of silanol, siloxane and silica-carbon also found at xerogels derived from silica with added by citric acid, but different calcination via air condition [36].

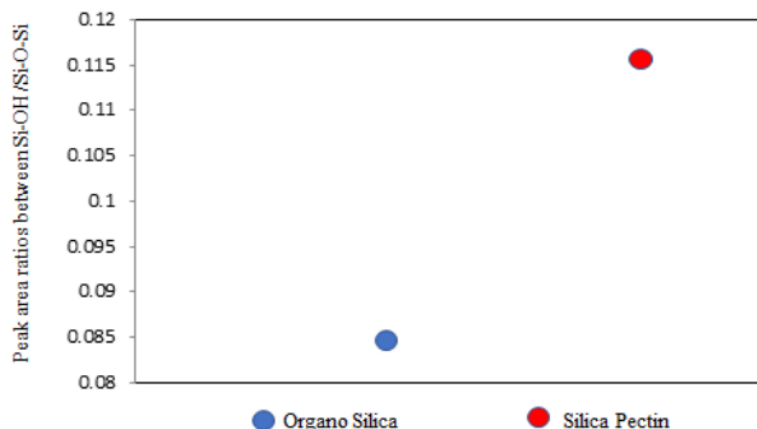


Figure 4. Peak area ratios between Si-OH/Si-O-Si and xerogel types

As shown in Fig. 4, Fityk software is used to investigate the effect of silica pectin addition to peak area. As presented by Fig. 4, the peak area ratio of silanol groups versus siloxane groups (Si-OH/Si-O-Si) was analysed. The result shows the lower ratio for organo silica xerogel sample which has the same calcination temperature as silica pectin template xerogel sample. It was expected that in silica pectin template xerogel, the nitric acid as a carbon source was decompose at such temperature and remain silanol as well as siloxane in the silica matrices [37]. The highest area ratio of silica pectin template indicates the high surface area of silanol or seems that the bonding of Si-OH was higher than SiO-Si. Otherwise, the lowest ratio of organo silica indicates the Si-OH bond was lower than Si-O-Si bond. However, the carbon chains bonding in the silica pectin materials were influenced by the temperature of calcination. Table 1 shows the different optimum condition in each calcination temperatures. The higher calcination temperature, the quicker evaporation process. It then creates the matrices become dense. Meanwhile, at high calcination temperature might cause carbon decomposition easily. Hence, the right/optimum calcination temperature is important to achieve the maximum results. Hence, it shows that the peak area ratio between SiOH and Si-O-Si (Si-OH/Si-O-Si) for silica pectin xerogel is also higher than organo silica, it is 0.085 and 0.116. Silica pectin is known as robust material due to the evaluation of functional groups. Despite of those result, the fabrication of silica sols applying catalyst through sol gel process was successful and promising potential application in desalination.



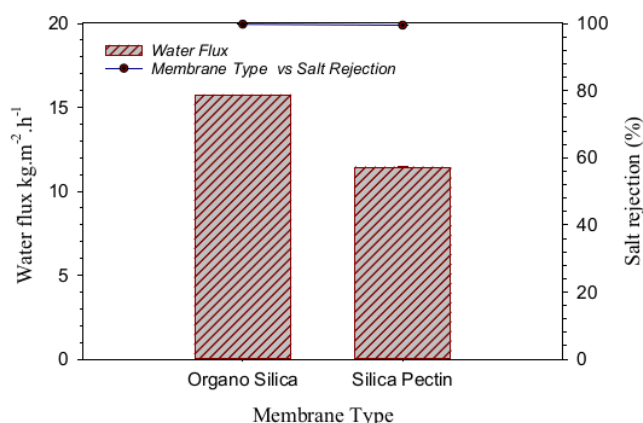


Figure 5. Membrane Performances of Organo Silica and Silica Pectin

Fig. 5 shows water flux and salt rejection, both organo silica and silica pectin, have relatively high salt rejection and water flux. The results showed that the water flux of organo silica and silica pectin membranes calcined under vacuum were  $15.74 \text{ kg.m}^{-2}.\text{h}^{-1}$  and  $11.44 \text{ kg.m}^{-2}.\text{h}^{-1}$ , respectively. The highest water flux is found in the organo silica membrane. The membrane salt rejection by vacuum calcination which has been tested with NaCl 0.3% is 99.77% for organo silica and 99.48% for silica pectin. These results are consistent with previous studies which reported that silica-based membranes had good rejection capabilities and >99% salt rejection [21].

### Conclusions

Based on the results, both of organosilica membranes calcined in vacuum calcination have siloxane (Si-O-Si), silanol (Si-OH) and silica-carbon (Si-C) groups. The organosilica membrane (citric acid) prepared by inner coating has the highest performance ( $15.74 \text{ kg.m}^{-2}.\text{h}^{-1}$ ; 99.77%) for brackish water (NaCl 0.3%). The peak area ratio between SiOH and Si-O-Si (Si-OH/Si-O-Si) for silica pectin xerogel is also higher than organo silica, it is 0.085 and 0.116.

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