Membrane pervaporation performance applied for brackish water prepared by vacuum impregnation method

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Abstract. Coating method and number of membrane layer are crucial factors on membrane performance. Through a vacuum impregnation method allows a sol solution uniformly fill into membrane support and it is required only less solution. The aim of this study is to apply vacuum impregnation method through vacuum calcination and air calcination during fabrication of silica membranes and to investigate the effect of layer variations on silica membranes performance to apply for brackish water. The sol solution was made from TEOS as silane precursor, ethanol and dual catalysts (citric acid + ammonia). Alumina membrane support was coated by vacuum impregnation method and calcined the membrane under air and vacuum condition. From the FTIR result, it indicates that silica membranes calcined in air and vacuum calcination have Si-O-Si and Si-OH. The vacuum impregnation obtained smoother surface membranes. The silica membrane calcined via vacuum calcination performs excellent water fluxes and salt rejection of 22.01 kg.m\textsuperscript{-2}.h\textsuperscript{-1} and 98.98 %. If compare to silica membranes calcined in air, the water flux (19.11 kg.m\textsuperscript{-2}.h\textsuperscript{-1}) and salt rejection (98.75 %). It also found the two layers silica membrane is better than three layers for the membrane performance result.

1. Introduction

WHO which stand for the global organization concerning about world health states up to 15 % of human population in the world has difficulty to get clean water. The biggest issue around the world is water scarcity. Especially people who live in wetland areas, river is an important water source for their daily activities. The water becomes salty due to seawater intrusion into river [1], especially during rainy season [2]. So that, wetland saline water has an abundant amount so that it can be used as a source of clean water [3]. Currently, pervaporation is used for treat saline water into clean water through desalination. This high water salt content may impact the environment if it may not be treated [4].

Membrane technology is widely chosen to solve the problem of access to clean water because it has advantages that are eco-friendly, energy efficient, high efficiency and easy to operate [5]. Zeolite and
silica are types of membranes that are often used in desalination [6, 7]. Membranes used are generally composed of a porous material-thin-film-medium that functions to separate particles with a specific molecular size from the solution [2, 8, 9].

Silica membrane has several advantages, namely high molecular sieving when compared to zeolite membrane [6], resistant with high temperatures [10] and have a good performance [11]. This unique properties can be applied to remove the salt particles in the water [11, 12]. In addition, it has a pore size ranging from 3-5 Å according to the size of the water kinetics diameter (\(dk = 2.6\) Å) [6]. However, it can block the hydrated salt ions (Na+ \(dk = 7.2\)Å) and Cl in the desalination process [13].

Many coating methods on membranes have been introduced such as dip-coating [14–20], electrospinning [21] and vacuum impregnation [22, 23]. Non-destructive method for presenting a solution of a certain composition into a porous matrix it is called vacuum impregnation. Mechanically induced difference pressure can transpires the mass transfer in vacuum impregnation [24]. Currently, the vacuum impregnation method is getting attention by researchers because it can minimize the possibility of physical damage to the membrane and can save membrane coating time [22, 25]. The structural formation of membrane can be easily control through vacuum impregnation [23].

Other parameters that can also affect the membrane performance are the number of membrane layers and calcination process [26]. Therefore, the aim of this research is to compare a vacuum calcination and air calcination in a silica membrane fabrication through vacuum impregnation and to investigate the effect of layer variations (2 layers and 3 layers) on the performance of silica membranes to 0.3 % NaCl (brackish water) as feed.

2. Methodology

2.1. Preparation and characterization of pure silica xerogel
Silica sol synthesis ware carried out by sol-gel method employing tetraethyl orthosilicate (TEOS, Merck), ethanol 96 % (EtOH), the dilute nitric acid (0.00078 M, HNO₃, Merck) and ammonia (NH₃, Merck). solution diluted with ethanol. First, TEOS was added drop-wise into ethanol and stirred for 5 min in an ice bath subsequently added HNO₃ by drop it slowly within 15 min. Then the solution was refluxed for 1 hour at 50 °C on a hot plate. After that, add the base catalyst in the form of ammonia which has been diluted first by drop-wise and reflux continued for 2 hours at 50 °C. At the end of 3 h refluxing the pH of the sol is measured to show pH 5 or pH 6. Then, dry the sol-gel at 60 °C for 24 hours to obtain xerogel and then grind it t’o a powder and grind it into a powder. Xerogel was then calcined at 600 °C for 4 hours. Xerogel characterization using FTIR test (Fourier transform infrared spectrometer).

2.2. Membrane preparation and characterisation
The pure sols were firstly put into quartz tube. Then, thin film membrane was coated on membrane support alumina-based tubular (\(\alpha\)-Al₂O₃ \(\Phi\)E100 nm), using the pure sols via a vacuum impregnation method with a dwell time of 2 min. After the coating process on each layer of the membrane, it is then dried by air and vacuum calcination for 1 h. This step was conducted for 2, 3, and 4 time to get varied number of thin film layers by vacuum impregnation method. The final membrane were evaluate by pervaporation to desalination of saline water. Vacuum impregnation set-up presented in figure 1 below:
Figure 1. Set-up impregnation method.

The pervaporation process in this research is presented in figure 2. The membrane was installed by dead end system which the one side connected to a cold trap (immersed in liquid nitrogen) and another side connected to vacuum pump operating at 1.5 kPa. The feed solution used was made of sodium chloride (NaCl, Sigma-Aldrich) dissolved in deionized water at a concentration of 0.3 %wt and the temperature used in this research is room temperature ($\approx 25 ^\circ C$). The feed solution was stirring constantly at 500 rpm and recirculation to avoid the concentration polarization on the contact membrane side. The water flux, $F$ (kg m$^{-2}$ h$^{-1}$), can be calculated using the equation $F = \frac{m}{A \Delta t}$, where $m$ is the mass of permeate (kg) left in the cold trap, $A$ is the surface-active area (m$^2$) of the membrane and $\Delta t$ is the time measurement (h). The salt rejection, $R$ (%), can be calculated using the equation $R = \frac{(C_f - C_p)}{C_f} \times 100 \%$, where $C_f$ and $C_p$ are the feed and permeate concentrations of salt (wt%). The concentration of salt has a correlation with the conductivity of the solution, the conductivity is measured using a conductivity meter.

Figure 2. Set-up for membrane pervaporation.
3. Result and Discussion

This study, the sol-gel method in the process has chosen because it is the most effective, simplest, cheapest when compared to the other methods [27]. It can also easily modify the pore size of the membrane and its morphological structure. The addition of a two-step acid-base in a sol-gel solution results in a relatively combination of small and large structures called bottleneck pores [4]. Firstly, the sol gel process is done under acidic conditions that lead to the formation of many silanol groups. The final silica sol pH is 6, which the pH is above the isoelectric point limit (pH 1-3) of the silica bridges [28, 29]. In this pH, the siloxane bridges formed high concentration due to the silanol group is to be deprotonated participating in the polycondensation reaction [13].

The FTIR (Fourier Transform Infrared) spectrum in the region of 1400-750 cm\(^{-1}\) of the calcined xerogel sample at temperature of 600 °C through air calcination shows in Figure 3. The peak wavelength of 1080 cm\(^{-1}\) represents siloxane (Si-O-Si). While the initial peak at 973 cm\(^{-1}\) shows vibrations of the silanol (Si-OH) group. Previous study has reported that silanol and siloxane appeared in silica membranes calcined in air and vacuum calcination [13]. Silica material has a high resistance temperature up to 800 °C [30].

![Figure 3. Spectrum FTIR xerogel pure silica.](image)

Based on figure 3, FTIR spectrum of the pure silica xerogel has siloxane bonds [Si-O-Si] and silanol bonds [Si-OH]. Siloxane group is seen at wavelength of 1080 cm\(^{-1}\) while the silanol group is seen at a wavelength of 973 cm\(^{-1}\). According to Elma, Yacou, Diniz da Costa and Wang [6], a low silanol concentration and a high siloxane concentration appeared in pH 6 of sol. In addition, the sol gel with pH 6 showed a tendency to form combination of micropores and mesopores. This pore size pattern could hinder small particles in micropore, yet allow the water passed through the membrane because of mesopores presence. A high salt rejection and water flux might be achieved [14]. Silanol are hydrophilic so that it reacts with water and forms fouling. Thus, silica network is designed to configure siloxane (Si-O-Si) and silanol (Si-OH) group [19].

Pure silica membrane fabricated by vacuum impregnation both calcined under air and vacuum condition have a clean surface, shining surface and no damage as shown in figure 4. This is because porous alumina domains provide the ideal conditions to hindered the thermal stresses induced while sintering process [13]. Therefore, there is no defect and crack on top layer of the membrane. Both of calcination types resulting in white color’s membrane because it utilized the alumina as support. In our
study, the vacuum impregnation only required less volume of solution than dip-coating process. The silica thin film attached on alumina support resulting in shining surface.

Figure 4. Picture of membrane pure silica (a) air calcination 2 layers (b) air calcination 3 layers (c) vacuum calcination 2 layers and (d) vacuum calcination 3 layers.

Figure 5 illustrates all pure silica membranes calcined with vacuum or air have relatively high rejection and water fluxes. The result shows the membranes water fluxes calcined under vacuum in variations of 2 layers and 3 layers are 22.01; 16.72 kg.m⁻².h⁻¹, respectively. While membranes calcined with air in variations of 2 layers and 3 layers are 19.11 and 12.46 kg.m⁻².h⁻¹, respectively. The highest water fluxes are found in membrane with 2 layers for both vacuum and air calcination. The salt rejection of membranes via vacuum calcination that have been tested with NaCl 0.3 % are 98.75 % for 2 layers and 99.94 % for 3 layers. On the other hand, the membranes made by air calcination at 2 layers and 3 layers are 98.98 % and 89.49 %, respectively. It happened because of the compound of silanol and siloxane presence in silica matrix. These results are in line with previous studies that reported a silica-based membranes have a good rejection ability and salt rejection >99 % [31].

Figure 5. Membrane performance of (a) vacuum calcination and (b) air calcination.
4. Conclusions
Based on the results, pure silica membranes calcined in air and vacuum calcination have siloxane and silanol groups. All the silica membranes prepared through the vacuum impregnation obtained a shining surface because of the thin film attached on alumina support. The 2 layers of silica membranes via vacuum calcination (22.01 kg.m⁻².h⁻¹; 98.98 %) and air calcination (19.11 kg.m⁻².h⁻¹; 98.75 %) resulting in better performance than 3 layers for NaCl 0.3 % (brackish water). The highest water flux achieved from silica membrane calcined in vacuum and less membrane thickness.

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