ORIGINAL PAPER: FUNCTIONAL COATINGS, THIN FILMS AND MEMBRANES (INCLUDING DEPOSITION TECHNIQUES)



Pervaporation membrane for desalination derived from tetraethylorthosilicate-methyltriethoxysilane

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Abstract

Silica membrane synthesis from tetraethoxysilane (TEOS) and methyltriethoxysilane (MTES) was carried out using ethanolacetic acid solvent through a sol-gel process. The effects of TEOS-MTES mol composition of 100-0, 90-10, 75-25, 50-50, 25-75, 10-90, and 0-100 and calcination temperatures of 350 and 500 °C were studied. The water contact angle was used to examine the hydrophobicity of silica thin films. A close correlation between hydrophobicity and the presence of the Si–OH and C–H groups was obtained. Hydrophobicity was enhanced by increasing the C–H/Si–O–Si ratio and decreasing Si –OH/Si–O–Si ratio. Silica membrane material maintained hydrophobic properties up to 400 °C. Thermal stability went up with the rise in MTES content. All silica xerogels exhibited microporous character with decreased pore volume and surface area with lower TEOS content. The pervaporation technique systematically studied the TEOS-MTES silica membrane's desalination performance using various saltwater concentrations and feed temperatures. The TEOS-MTES composition played an essential role in determining the membrane's character and performance, salt rejection, and water fluxes. The high TEOS content led to high water flux. Alternatively, a high MTES content led to a high salt rejection. All membranes provided good salt rejection with values up to 99%, especially those with high MTES contents.

Graphical abstract



Keywords Silica membrane · Desalination · Pervaporation · Tetraethylorthosilicate (TEOS) · Methyltriethoxysilane (MTES)

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Highlights

- Silica membranes are synthesized using tetraethylorthosilicate-methyltriethoxysilane.
- There is a strong correlation between hydrophobicity with Si-OH and C-H groups.
- The silica membrane material maintained hydrophobic properties up to 400 °C.
- Precursor composition influences the performance of pervaporation desalination.
- Silica membranes produce high-salt rejection and good water flux.

1 Introduction

The population that impels demands for industrial and agricultural activities to afford consumption continues to rise from year to year, increasing the need for freshwater. Nevertheless, <3% of the water on earth is freshwater [1], and it is increasingly limited and reduced due to global warming and pollution. In contrast, about 97% of the water in the sea [1], which, due to high salt concentrations, cannot be used directly for daily, industrial, and agricultural needs. For this reason, a desalination technology to remove salt from seawater and generate freshwater is needed [2]. Among desalination technologies that have been widely used are thermal technology, chemical processes, adsorption, and membrane filtering [3].

Desalination converts saltwater into freshwater from an almost unlimited supply of seawater. Currently, the commercial desalination technologies exist are distillation and reverse osmosis (RO) [4]. RO membrane technology is widely used because it has high efficiency and is more economical than thermal desalination, stable operating processes, low material costs, easy integration with industrial systems, and is easy to control [5]. On the other hand, the disadvantage of RO membranes is that the process requires high pressure to counteract the osmotic pressure from saltwater concentrations and multi-level pre-treatment to prevent fouling [6].

A membrane technology ongoingly being developed is pervaporation (PV) [7]. In contrast with RO, which relies on pressure, PV carries out desalination through selective diffusion of feed solution molecules across the membrane due to differences in the diffusivity of each component in the feed phase. In the PV system, superiority is found in the difference in vapor pressure from the feed and permeate phases caused by the vacuum process [8]. Mass transfer in PV occurs through the adsorption-diffusion-desorption process, which consists of three stages: (1) adsorption of species on membrane surfaces, (2) diffusion of selected species through membranes, and (3) desorption of species as vapor on the permeate side [9, 10]. In so doing, the PV does not require high operating pressure, nor does it require initial multilevel treatment. PV has been shown to have high salt rejection (>99%), which does not depend on feed conditions [11]. However, the main challenge for PV is low water flux.

Silica with a pore size ranging from 3–5 Å could become a selective membrane for saltwater desalination. Silica, through

the PV mechanism, can be a selective separator between water molecules ($d_k = 2.6 \text{ Å}$) and hydrated salt ions (for example, Na⁺: $d_k = 7.2 \text{ Å}$ and Cl⁻: $d_k = 6.6 \text{ Å}$) [12], thus separating bulks of water from salt. Generally, silica membranes are synthesized using the sol–gel method because this process is easy and cost-effective [13]. Elma et al. [14] succeeded in making silica membranes by the sol–gel method using tetraethylorthosilicate (TEOS) as silica precursors in ethanol solution for PV. The results showed that the membrane had a salt rejection of up to 99% and could maintain desalination performance up to 250 h.

The silica structure consists of siloxane bonds (Si–O –Si) and hydrophilic silanol groups (Si–OH) and, in the presence of water, can be hydrolyzed [15]. Hydrolysis occurs because the silanol group reacts with water and causes damage to the silica structure, leading to the implication of reduced separation performance and, ultimately, decreased desalination quality. Some research on the synthesis of silica membranes for desalination used TEOS as a precursor to silica [16, 17]. TEOS is widely used as a silica source because it has proven excellent in producing silica polymer frameworks. However, due to its hydrophilic nature, TEOS is usually modified with other materials to increase the hydrostability of the resulting silica polymer.

Several strategies have been developed to address the silica hydrostability problem: First, insert an organic template that is not bound to silica into a pure silica matrix [18, 19]. The presence of carbon groups in the silica matrix can prevent silica groups' mobility from hydrolytic attack [20]. Elma et al. [11] fabricated silica membranes with the Pluronic@P123 carbon templates and produced membranes with outstanding performance. Second, the combination of terminal alkyl groups (Si–CH₃ or other Si-R) using various precursors during sol–gel synthesis [21]. In this approach, bridged organosilane (R'O)₃Si-R-Si(OR')₃ can be used, one of which was 1,2-Bis (triethoxysilyl) ethane [22]. Third, the addition of metal oxides such as cobalt [23], iron [24], and nickel [25] in which the membranes produced by the latter exhibited a salt rejection of up to 99.9%.

Methyltriethoxysilane (MTES) is a compound that demonstrates hydrophobic nature. MTES has a low dipole moment and low surface energy of 1.38 mJ/m^2 [26]. MTES based coatings exhibited transparent superhydrophobicity with a water contact angle (WCA = $153 \pm 3^\circ$) for the highest deposition temperature. The stability test showed that this superhydrophobic coating material has excellent

thermal stability (weight loss = 0.429 wt%) in a nitrogen gas medium [27]. Meanwhile, our previous study [28], showed that changing the pH from acid to base increases the surface hydrophobicity, and the MTES silica film can maintain hydrophobic properties up to 420 °C. Li et al. [29] prepared an antireflective coating (ARC) by sol–gel method using MTES. The ARC shows a hydrophobic surface with the highest WCA of 126.53°.

On the other hand, Li et al. [30] prepared a modified SiO_2 gel coating filter material with TEOS and MTES. The results showed that SiO_2 nanoparticles formed on the surface after finishing, and the surface was covered with hydrophobic methyl groups after modification with MTES. The hydrophobic nature of the material was significantly increased, and the WCA of the surface reached 154.11°. Research on the synthesis of SiO_2 antireflection coatings from TEOS and MTES also showed that the WCA reached 118°, and the light transmittance in the entire spectrum reached 95.95%.

Although efforts have been made to increase silica hydrostability by adding terminal alkyl [21], however, there are still few reports on the use of the dual precursor TEOS-MTES for separation, some of which are for gas separation [31], molecular separations [32] but the authors have not found for desalination applications. In this study, silica membrane preparation was carried out using the dual precursors of TEOS and MTES, wherein the presence of MTES is expected to improve the hydrophobic nature of the resulting silica material. The effect of the TEOS-MTES ratio on the resulting silica character is explained. The TEOS-MTES silica membrane performance in brine desalination through the PV process is also studied.

2 Methodology

This research involves stages of (1) xerogel and silica thin layer syntheses, (2) characterization of TEOS-MTES silica xerogel using Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analyzer (TGA), gas sorption analysis (GSA), and measurement of WCA on the silica layer, and (3) measurement of the TEOS-MTES silica membrane performance on saltwater desalination through PV.

3 Preparation of silica xerogel and thin film

The TEOS-MTES solution was prepared using a solution of ethanol-acetic acid (0.25 M acetic acid in ethanol) to obtain pH = 5. The TEOS and MTES precursors were added to the ethanol-acetic acid solution to obtain a molar ratio of silica precursors: ethanol-acetic acid

solution of 1:50 and stirred using a magnetic stirrer for 30 min. The compositions of TEOS-MTES were varied with percent ratios of 100-0, 90-10, 75-25, 50-50, 25-75, 10-90, and 0-100. The mole ratio of silica precursors to the solvent was fixed for all TEOS-MTES compositions. Subsequently, the resulting solution was divided into two parts. The first part was dried at room temperature to produce xerogels for characterization purposes, and the second part was coated onto ceramic plates and membrane support. Xerogel was made by evaporating the solution at room temperature followed by drying it in an oven at 60 °C under normal atmospheric conditions. Xerogel samples were crushed and sieved with 100-mesh (150 microns) sieves and then calcinated at 350 and 500 °C for 30 min with a 2 °C min⁻¹ heating rate.

The silica thin layer was prepared by the dip-coating of the commercial ceramic plates and alumina supports (α -Al₂O₃ tubular substrates (Φ pore size \approx 100 nm), Ceramic Oxide Fabricates) into TEOS-MTES solution for 1 min, later dried at room temperature. The coated ceramic plates and alumina substrates were then calcined with the xerogel's temperature and heating rate. The series of dip coating, drying, and calcination was repeated up to four times.

4 Characterization

The functional groups of the silica xerogels were analyzed on dry samples using a Shimadzu IRAffinity-1 FTIR spectrometer with a Pike MIRacle single-bounce diamond attenuated total reflectance attachment. FTIR spectra were collected at a resolution of 1 cm^{-1} in the range of 4000–600 cm⁻¹ for a total of 32 scans and were not corrected for penetration depth variation. Thermal analysis for silica xerogels was carried out using a Mettler Toledo TGA/DSC 1 TGA with large furnaces in a standard atmosphere with an airflow of 60 ml min⁻¹ and a heating speed of 2 °C min⁻¹ over the range of 30–800 °C. Analysis of nitrogen adsorption and desorption was performed using Micromeritic TriStar 3020 surface area and porosity at 77 K (-196 °C) after the samples (~ 0.2 g) were degassed by vacuuming (10^{-6} mbar) for more than 6 h at 125 °C before analysis. Pure N2 (99.9%) gas was used. Porous properties were determined by analyzing the N₂ adsorption/desorption data using MicroActive Software for TriStar 3020. The specific surface area was determined using the Brunner-Emmett-Teller (BET) method in the relative pressure range $0.05 < P/P^{\circ} < 0.25$. The total pore volume was taken from the last point of the isotherm. The average pore diameter was calculated with 4 V/A from the BET value. Pore size distribution (PSD) was estimated by the MP Method. WCA was measured using the tangent $\theta/2$ method described in [33]. Water was dropped on the surface of the ceramic plate



Fig. 1 a WCA on TEOS-MTES silica thin layers coated on ceramic plates calcined at 350 $^\circ$ C, **b** relationship between the TEOS-MTES composition and WCA

using a syringe. Next, water drops were photographed using a Samsung Galaxy A5 camera. The WCA average value was obtained from three points, dripped onto different positions on the same plate. The surface morphology of the TEOD-MTES thin film was imaged using a Phenom Pro X desktop SEM scanning electron microscope (SEM) operated at an accelerating voltage of 10 kV where deep prepared samples at various TEOS-MTES ratios were placed on clean aluminum stubs.

5 Desalination performance testing

The measurement of desalination performance for silica membranes was undertaken by measuring the water flux and salt rejection according to the formula described elsewhere [9]. The membrane assembly referred to a classic PV design as described in [14, 25]. The membrane on its tubular support was immersed in a glass containing a sodium chloride (NaCl, Sigma Aldrich) solution with concentrations varying from 0.3, 1, and 3.5% with water temperatures of 15, 30, and 45 °C in which one end of the tube support was blocked. Whereas the other end was connected to a cold trap (immersed in an ice bath) and a vacuum pump at 1.5 kPa. The salt concentration was determined using a total dissolved solids meter referring to the standard curve.

6 Results and discussion

In this section, the hydrophobic character of TEOS-MTES silica xerogels and the thin films will be discussed predicated on the FTIR, TGA, and GSA data, followed by a discussion on the performance of desalination through the PV process.

7 Hydrophobicity of silica thin layer

The TEOS-MTES silica film coated on a ceramic plate and calcined at 350 and 500 °C interactions with water droplets as indicated by the shape of the water droplets is presented in Fig. 1.

Figure 1 shows that with the increase in MTES content in the TEOS-MTES silica thin layer, the shape of the water droplets was bigger and more spherical, both at calcination temperatures of 350 and 500 °C. Initially, water droplets on the uncoated ceramic plate's surface showed a low contact angle, which indicated that the ceramic plate was hydrophilic. The presence of the silica thin layer significantly increased the hydrophobicity of the surface of the ceramic plate. Moreover, the sizes of the water droplet spheres at the calcination temperature of 350 °C were always larger than its counterpart at 500 °C for the entire TEOS-MTES composition. This indicates that the hydrophobic nature of the calcined silica thin layer at 500 °C is always lower than that calcined at 350 °C. This expresses that part or all the methyl groups have been lost due to heating at 500 °C. According to Yu et al. [34], the maximum calcination temperature of MTES in maintaining its hydrophobic nature is 350 °C. When the calcination temperature is above 350 °C, the hydrophobic nature of MTES declines and transforms to be more hydrophilic. Thus, it can be concluded that the composition of TEOS-MTES and calcination temperature affect the hydrophobic character of the resulting silica thin film.

The TEOS-MTES composition significantly affects the WCA magnitude formed both at calcination temperatures of 350 and 500 °C. The TEOS-MTES composition of 0-100 had the highest contact angles, 87.46° at 350 °C and 74.05° at 500 °C. Alternatively, the TEOS-MTES composition of 100-0 had the smallest contact angles, 66.12° at 350 °C and 43.28° at 500 °C. WCA enlarged with the increase of MTES content in the silica matrix. According to Wang et al. [35], the low surface energy of organic silicon compounds results in a more hydrophobic character of a material. The increase in MTES content in the silica thin layers reduced the surface energy and enhanced the hydrophobic properties of silica thin layers.

Apart from the TEOS-MTES composition, the calcination temperature also affects the WCA formed. Increase in WCA was higher at calcination temperature of 500 °C than 350 °C as indicated by the slope values, which were steeper at 500 °C with a slope value of 0.288 compared to 350 °C with a slope value of 0.189. It is most likely that at 500 °C calcination, the silica xerogel has a hydrophobic steering group more evenly distributed on the ceramic plate's surface compared to that calcined at 350 °C. The slope values were also proportional to the R^2 values, where at 500 °C calcination, the R^2 was 0.934, while at 350 °C, it was 0.890. These results indicate a close correlation between the MTES content and WCA, especially at a 500 °C calcination temperature.



Fig. 2 FTIR spectra of silica xerogels calcined at 350 and 500 °C with TEOS-MTES ratios of (a) 100:0; (b) 90:10; (c) 75:25; (d) 50:50; (e) 25:75; (f) 10:90; (g) 0:100

8 Functional groups and bond types of silica xerogels

The functional groups and bond types of silica xerogels were identified using FTIR. The FTIR spectra in the wavenumber range between 700 and 1400 cm^{-1} of the TEOS-MTES silica xerogel with various compositions are presented in Fig. 2. No

peaks appear after 1400 cm^{-1} , except for wide and low peaks at 3500 cm^{-1} originating from water molecules. As the silica framework peaks are between $700-1400 \text{ cm}^{-1}$, only these wavenumbers are presented here.

Figure 2 presents FTIR spectra with the typical shape of a silica framework. In general, the functional groups and bond types in the TEOS-MTES silica xerogel can be classified into three components, i.e., the silica polymer framework of Si-O -Si (siloxane), the Si-OH (silanol) group, and the Si-CH₃ (methyl) group originating from MTES [33]. Siloxane and silanol vibration bands are always found in calcined silica xerogels and represent the final stage of sol-gel synthesis, denoting the hydrolysis reactions that produce silanol groups and condensation reactions that produce siloxane bridges. The strong absorption peak at 1270 cm^{-1} is the symmetrical vibration (v_s) of the C-H group [36], while the peak at 760 cm^{-1} corresponds to the symmetrical vibrations (v_s) of the Si-C group [37]. For both CH and Si-C groups, the adsorption increased with increasing MTES content in the silica matrix. These peaks confirm the presence of the CH₃ group from MTES in silica xerogel.

The strong peak in the region of 1000–1200 cm⁻¹ centered at 1070 cm⁻¹ is an asymmetric vibration bond (v_{as}) of Si–O –Si representing the silica network structure [38, 39]. The peak shows the success of chemical gelation between TEOS and MTES. The Si–O–Si peak shifts toward smaller wavenumbers (blue shift) with increasing MTES content in the sample. The Si–O–Si bond and the Si–CH₃ group contribute to the hydrophobic character of the silica polymer.

The weak shoulder-type peak observed at 960 cm^{-1} is due to asymmetrical stretching vibrations (v_s) of the Si–OH group, which also experienced a blue shift. The Si-OH group contributes to the hydrophilic character [40]. This peak is observed in uncalcined xerogels, and its intensity decreases with increasing MTES content. There is a seesaw phenomenon in that when the hydrophobic organic (methyl) content rises, the hydrophilic Si-OH group decreases and vice versa. Moreover, the shoulder peak at 960 cm^{-1} was not seen in the xerogel calcined at 500 °C. This suggests that the calcination process up to 500 °C forces the remaining Si-OH groups to fold further to produce Si-O-Si. The spectral shape and peak intensity of uncalcined and calcined silica xerogels at 300 °C tend to be similar but slightly different at 500 °C. The C-H peak at 1270 cm^{-1} and the Si-C group at 760 cm^{-1} re-reduced dramatically at the calcination temperature of 500 °C. This indicates that the thermal stability of TEOS-MTES silica is at least up to 350 °C, and the calcination process at 500 °C causes loss of methyl groups in the silica framework.

To determine the influence of the functional groups quantitatively, FTIR spectra in the $900-1300 \text{ cm}^{-1}$ region were deconvolved using Fityk software to obtain the derivative curves that compose the spectra through the Gaussian



Fig. 3 Deconvolution of FTIR spectra from TEOS-MTES silica xerogel of 10-90 ratio calcined at 350 $^{\circ}\mathrm{C}$

Table 1 The deconvolution peaks of FTIR spectra referring to [33]

Derivative Peak	Wavenumber (cm ⁻¹)	Functional group	
1	960	Si-OH stretching vibration	
2	1010	linear Si-O-Si	
3	1060	cyclic Si–O–Si [52]	
4	1100	asymmetrical stretching vibrations of Si–O–Si [53]	
5	1140	longitudinal (LO) optical mode Si–O–Si	
6	1270	C-H group [36]	

approach. The intensity of the siloxane peak at ~ 1050 cm^{-1} was normalized to 100% for each spectrum. The deconvoluted curve is presented in Fig. 3. Initially, the FTIR curve was normalized, and the 1080 cm⁻¹ peak was made 100% for all spectra analyzed. A derivation curve from one of the samples (in this case, TEOS-MTES silica of 10:90 and calcined at 350 °C) was used as a reference, and six derivative peaks were obtained. Subsequently, all FTIR spectra were deconvolved, referring to the set reference with the value of Half width at half maximum for each derivative peak made constant.

Each derivative curve represents one functional group and is presented in Table 1. The derivative curve areas can be compared to determine the quantitative comparison of functional groups.

From the deconvolution, the area of each derivative peak can be derived. According to the ratio of (C-H)/(linear Si-O-Si) (peak area number 6 divided by peak area number 2) and the ratio of (Si-OH)/(linear Si-O-Si) (peak area number 1 divided by peak area number 2) were calculated. Peak number 2 was made the denominator because it is the highest peak and represents the main silica framework and the normalization reference. The relationships between the ratio of (C-H)/(linear Si-O-Si) and the ratio of (Si-OH)/(linear Si-O-Si) to the TEOS-MTES compositions are presented in Fig. 4.

Figure 4 shows that the C-H group content heightened with increasing MTES content in the silica matrices at 350 and 500 °C. This is easily understood as an increase in the content of MTES will certainly increase the amount of C-H groups. The C-H group was consistently higher in the silica xerogels calcined at 350 than 500 °C for all composition variations. The C-H group's slope on the 350 °C calcined xerogels rose sharply, while at 500 °C, the rise was observed to be relatively gentle. This implies that the C-H group was burned out due to the calcination at the higher temperature of 500 °C. On the other hand, the (Si-OH)/(linear Si-O-Si) ratio diminished with increasing MTES content due to the upsurge of the Si -CH₃ group. It is thought that the Si-CH₃ group obstructed the Si-OH group in xerogel. The (Si-OH)/(linear Si-O-Si) ratio descended steeply at 350 °C calcined silica and tended to be declivous at 500 °C. This is possible as at 350 °C, there were still many Si-CH₃ groups blocking Si-OH groups. In contrast, at 500 °C, as the amount of Si-CH₃ was small, the change in the number of Si-OH groups became insignificant.

The contact angles measured in this study were directly proportional to the composition of the MTES. Accordingly, the relationships between the (C-H)/(linear Si-O-Si) ratio and (Si-OH)/(linear Si-O-Si) ratio with WCA were made and are presented in Fig. 5. The increase in WCA is proportional to the increase in the (C-H)/(linear Si-O-Si) ratio but inversely proportional to the increase in the (Si-OH)/(linear Si-O-Si) ratio for both calcination temperatures. Although the correlation is not too linear, it proves that silica thin layers' hydrophobic properties are directly proportional to the number of $Si-CH_3$ groups and inversely so to the number of Si-OH groups.

9 Thermal properties

A thermal stability analysis was performed using TGA to determine the thermal stability achieved by the TEOS-MTES hydrophobic silica xerogel. The results are shown in Fig. 6.

Figure 6a, b shows an increase in the MTES content decreases thermal stability. This can be discerned from the reduced temperature required for the decomposition to occur and the decrease in the percentage of weight loss. In general, the weight loss of silica xerogels occur in four stages, i.e., at temperatures of (1) 30–130 °C, (2) 130–400 °C, (3) 400-550 °C and (4) 550-800 °C. In the first stage, the weight loss comes from the evaporation of solvents and volatile molecules present on the surface and in the pores [41, 42]. The weight reduction is significant because there are residual ethanol solvent and water present from the condensation reaction. In the first stage of mass reduction, the largest occurred in the TEOS-MTES composition of= 100-0, which was about 25%, followed by reductions of 19, 18, and 12.4% for variations of 90-10, 75-25, and 50-50. At high MTES content, the sample mass tended not to change much (<10%).



Fig. 4 Relationships between the TEOS-MTES compositions to a (C-H)/(linear Si-O-Si) ratio and b (Si-OH)/(linear Si-O-Si) ratio



Fig. 5 Relationships between a the (C-H)/(linear Si-O-Si) ratio and b the (Si-OH)/(linear Si-O-Si) ratio with the WCA



Fig. 6 TEOS-MTES silica xerogel a Thermogravimetric and (TGA), b derivative thermogravimetry (DTG) analysis for ratios of (a) 100:0; (b) 90:10; (c) 75:25; (d) 50:50; (e) 25:75; (f) 10:90; (g) 0:100

For TEOS-MTES of 10-90, the weight loss was only 1.2%. This is considerably less than ~ 25% for TEOS-derived samples only. The considerable reduction in mass at the high TEOS content can be attributed to the fact that TEOS carries many silanol groups, which act as large adsorption centers for water and other polar molecules. The magnitude of the change in mass indicates that xerogel hygroscopicity decreases with increasing MTES content [41, 43] due to the decrease in the content of OH groups, as described in the FTIR section. On the

other hand, Fig. 6b illustrates that as the MTES content increases, the temperature required to release ethanol, water, and volatile molecules shifts to a lower temperature. The effect of MTES content on thermal properties is regular, as indicated by the shrinking of the peaks in the 30–130 °C region and the gradual enlargement of the peaks in the 430–530 °C region as shown in Fig. 6b.

The second stage of mass reduction is between 130-400 °C. At this stage, there was a relatively small





mass decrease in all TEOS-MTES variations due to the release of water and other solvents trapped in the pore. Some of the Si–C group decomposed slightly, and a further condensation reaction of Si–OH occurred, forming Si–O–Si. The largest mass reduction for this stage occurred at the TEOS-MTES ratio of 100-0, which was 6%, as it has more Si–OH groups than the other samples. For the other TEOS-MTES compositions, the mass reductions were below 5%.

The third stage is at 400–550 °C, where high mass reductions in xerogels with varying MTES contents were observed to be more than 50%. Figure 6a shows that the higher the MTES content, the greater the percentage of mass reduction. At this stage, the CH_3 group

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decomposition reaction occurs. This explains why the hydrophobic properties of the film were drastically reduced and became more hydrophilic. TEOS-MTES silica can retain its hydrophobic properties up to a temperature of 400 °C. Figure 6b shows that at the TEOS-MTES ratio of 100: 0 (curve a) and 90:10 (curve b), no CH₃ decomposition peaks appeared. However, starting from the TEOS-MTES ratio of 75:25 (curve c), the peak of the CH₃ decomposition is pronounced. The increase in the peak of CH₃ decomposition was inversely proportional to the loss of volatile molecules in the first stage. With the increase in the MTES content, the decomposition of CH₃ occurred at lower temperatures, but quantitatively, the amount raised, indicated by the larger peak



Fig. 8 N₂ adsorption isotherms from TEOS-MTES silica xerogels calcined at **a** 350 °C, **b** 500 °C, (a) 100:0; (b) 90:10; (c) 75:25; (d) 50:50; (e) 25:75; (f) 10:90; (g) 0:100

area. There was no noticeable weight loss in the last stage of mass reduction at 400-550 °C, indicating that the silica framework formation had become stable.

9.1 Scanning electron microscopy

Two-dimensional morphological studies of hydrophobic silica thin films were carried out using scanning electron microscopy. The surface morphologies of the DMDM-TEOS silica film at various pH coated on alumina substrates are presented in Fig. 7 at $\times 10,000$ magnification. The SEM image shows that the silica film is not homogeneous. As the pH increased, the changes in the fracture morphology of the silica thin films became more clearly visible. With increasing pH, a different texture appears on the surface of the coating. At acidic pH, silica tends to be finer, with fewer cracks on the surface. However, as the pH increases, the silica grains tend to become more numerous and smaller, resulting in a rougher surface.

According to the wetting theory proposed by Cassie and Baxter [44], surface roughness is one of the main factors for achieving hydrophobicity. Therefore, low surface energy is mainly caused by hydrocarbon derivatives combined with hydrophobic surface roughness [45]. According to Wenzel, surface roughness increases solid surface area, which geometrically results in increased hydrophobicity. In the Cassie approach, it is stated that air can be trapped under droplets, which leads to hydrophobic behavior because water droplets are partially above the air. Figure 7 shows the silica coating made at alkaline pH, presenting higher surface roughness, reducing the optical loss produced at acidic pH.

A cross-sectional view is presented in Fig. 7f. SEM images with $\times 500$ or $\times 2500$ magnification (not presented in figure) do not clearly show the thickness of the silica layer. The SEM image only shows a cross-sectional image of the alumina substrate. This indicates that the

silica layer formed is very thin and, on a nanometer scale. Previous studies [46–48] report that the thickness of the silica layer is in the range of 200 nm. In this study, the dip-coating and calcination processes were also carried out four times, so it is assumed that the thickness of the silica thin layer is also around 150 nm. Another thing that may happen is that the silica layer enters the pores of the alumina.

10 Pore and surface characters

The nitrogen adsorption isotherms for the TEOS-MTES silica xerogels of all compositions at calcination temperatures of 350 °C (a) and 500 °C (b) are presented in Fig. 8. All adsorption isotherms exhibit Type I characters, which imply that silica xerogel is microporous. The quantity of adsorbed nitrogen is relatively high at a low relative pressure (P/P° < 0.2). This indicates the presence of strong adsorption of the surface of silica towards nitrogen. For P/P ° > 0.2, nitrogen adsorption tended to remain because the silica xerogel surface had been saturated.

The quantity of nitrogen adsorbed decreased gradually with increasing MTES content in the silica xerogels, implying a decrease in pore volume. Even for the TEOS-MTES composition of 25:75 to 0:100, the amount of nitrogen adsorbed was small, indicating low pore volumes. The outcome is probably due to the presence of CH_3 groups constricting the pores. Figure 8b shows that the nitrogen adsorbed dropped dramatically at the higher calcination temperature (500 °C). Xerogels with more TEOS content (samples a, b, and c) still showed nitrogen adsorption, but for xerogels with more MTES content (d, e, f, g), nitrogen adsorption was deficient.

The BET surface area, pore-volume, and average pore size of calcined silica xerogels at 350 and 500 °C are presented in Fig. 9. It can be highlighted that the BET surface



Fig. 9 BET surface area, average pore volume, and average pore size of TEOS-MTES silica xerogel calcined at a 350 °C and b 500 °C



Fig. 10 The schematic reaction between TEOS and MTES under TEOS-rich and MTES-rich conditions

area and pore volume decreased with increasing MTES content in the silica xerogels and were highly dependent upon the TEOS-MTES composition. It is observed that there was more than a 50% reduction in both parameters from the TEOS-MTES compositions of 100:0 to 50:50. Such can be attributed to the CH₃ groups from MTES present on the surface of the pore tunnel, causing micropore clogging. This pore narrowing increased with increasing MTES content in the silica matrix. Surface area and pore volume for samples prepared with an MTES content of more than 50% were low. Figure 9a, b shows that the curves of the two parameters coincide for both calcination temperatures, showing a uniform pore size for the entire TEOS-MTES compositions. The pore sizes for calcined xerogels at $350 \,^{\circ}\text{C}$ were $25 \pm 6 \,^{\text{A}}$ while those calcined at $500 \,^{\circ}\text{C}$ were $38 \text{ \AA} \pm 23 \text{ \AA}$ exhibiting a higher average deviation. In addition, the BET surface area and pore volume also decreased with increasing calcination temperature. For example, in the TEOS-MTES silica xerogel with a 100:0 ratio, there was a decrease in the BET area from $465 \text{ m}^2 \text{ g}^{-1}$ (at 350 °C) to 297 m² g⁻¹ (at 500 °C), or a decrease in surface area by 30%. This occurred due to the silica structure's densification at a higher temperature, which is in line with the TGA results.



Fig. 11 Pore size distributions of TEOS-MTES silica xerogels calcined at 350 $^{\circ}\mathrm{C}$

Increasing MTES content in solution causes the Si–O–Si as the main silica framework to be less produced. TEOS-rich solutions are easy to produce Si–O–Si framework since TEOS has 4 Si–O groups which are easy to bond with each other. In contrast, in MTES-rich solution, the CH₃ group in MTES inhibits the formation of the Si–O–Si framework, but on the other hand, makes more Si–CH₃ groups. The schematic reaction between TEOS and MTES is presented in Fig. 10.

The lack of Si–O–Si and the large amount of Si–CH₃ in the framework causes the silica structure to become more brittle, more prone to collapse, and easily densify with increasing temperature.

Figure 11 shows the PSD of a silica xerogel sample, calcined at 350 °C based on the MP method. The *Y*-axis shows that pore volumes are seen in silica xerogels with high TEOS content, and they lessen with increasing MTES content. All samples showed dominant peaks in the micropore area with the highest pore volume at a radius of 0.3 nm (3 Å) or a pore diameter of 6 Å. These values are much lower than the average pore size of 25 Å, indicating that most pores are in micropore sizes below 7.5 Å.



Fig. 12 Desalination performance at salt concentrations of a 0.3%, b 1%, c 3.5% and feed temperatures of 15 °C (•), 30 °C (•), and 60 °C (•)

11 Desalination performance

All experiments were carried out by PV using a silica membrane with brine in the feed. The temperature stability of the feed was controlled so that the driving force and transmembrane pressure were constant (Fig. 12).

Figure 12 shows the performance of the membranes in the PV desalination. The water flux and salt rejection values of various TEOS-MTES silica membranes are presented as a function of feed temperature and salt concentration. Three trends can be observed regarding the membrane performance for desalination. The first is the decrease in water flux with increasing MTES content in silica, though simultaneously increasing salt rejection. Indeed, there is always a seesaw between quantity (water flux) and quality (salt rejection). When salt rejection increases, at the same time, freshwater production decreases and vice versa. Salt rejection of more than 98% was observed for 10-90 TEOS-MTES membrane at feed temperatures of 15 and 30 °C regardless of salt concentration. For membranes with higher TEOS contents, salt rejection decreased to 95% at 15 and 30 °C, although this performance was still considered very good. High water flux in silica membranes with dominant TEOS content is related to the total pore volume of silica, giving access to more water vapor, as discussed in Figs. 9 and 10. It can be seen that the

10-90 TEOS-MTES membrane, analyzed at the temperature of 30 °C and 1% water concentration, had a salt rejection of up to 98%, but the water flux was only $2 \text{ kg m}^{-2} \text{ h}^{-1}$. Meanwhile, in the 90-10 TEOS-MTES membrane, salt rejection decreased to 96.5%, but water flux increased to $4.4 \text{ kg m}^{-2} \text{ h}^{-1}$. Interestingly, the material was more hydrophobic due to the high content of the CH₃ group, showing a higher selectivity. This happens because hydrophobic material can reduce pore wetting [49], so water vapor moves faster than hydrated salt ions. However, the water flux observed is found to be the opposite of this opinion. The presence of CH₃ groups has the advantage of reducing the surface wetting, but on the other hand, it has the disadvantage of pore-narrowing. The membrane that contains more MTES in the silica matrix also adsorbs fewer water molecules, causing the flux to decrease.

The second trend is the slight decrease in flux with the increasing concentration of the salt solution. This is due to the affinity of the silica surface, which attracts hydrated ions [50]. According to Han and Peng [51], the size of hydrated ions from Cl^- and Na^+ are 6.64 and 7.16 Å, respectively, and these are much larger than the kinetic diameter of water (2.6 Å) [12]. This means that with a dominant pore diameter below 7.5 Å, higher salt concentrations are more at risk of causing silica pore narrowing. This, in turn, prevents water molecules from diffusing through the membrane. The effect

Membrane type	Feed temp. (°C)	Feed concentration (%)	Water flux $(\text{kg m}^{-2} \text{h}^{-1})$	Salt rejection (%)	Ref.
TEOS-MTES silica membrane	15–45	0.3–3.5	2–5	>98	This work
Si-P123 calcined at 350 °C	25-60	0.3–5	1.1–5.6	99.2	[54]
Hybrid membrane	25-60	1–15	2.3–5.7	>99.7	[55]
Carbonized C16 silica template	60	0.3-3.5	2.1-3.1	91–97%	[18]
Hybrid TEVS-P123	60	0.3	3.7	>95	[56]
Silica-cobalt	22-60	0.3-7.5	0.6-25.8	>90	[23]
PTFE membrane	85	12%	5	>99	[57]
PVDF membrane	65	7.5	9.5–10.8	>99	[58]

Table 2 Desalination performance of several membrane types

has previously been reported for silica membranes [23] related to concentration polarization. However, in this study, an increase in the saltwater concentration did not significantly reduce the resulting water flux and selectivity. This indicates that the TEOS-MTES silica membrane is potential enough to be used as a desalination membrane for various salt concentrations.

The third is the increase of water flux with increasing salt solution temperature for all TEOS-MTES compositions and salt solution concentrations. For example, the water fluxes, measured at 15, 30, and 45 °C at 1% feed salt concentration for the TEOS-MTES of 90-10 membrane increased respectively from 3.93 to 4.40 and then to $4.87 \text{ kg m}^{-2} \text{ h}^{-1}$. Since PV exploits the difference in vapor pressure between the feed phase and the permeate phase, the higher temperature causes the vapor pressure in the feed phase to increase, increasing the salt solution's driving force. This condition is expected in the PV process. This is, of course, a weakness of PV, where to produce higher fluxes, higher heat is needed.

Table 2 summarizes this study membrane's performance and other membranes synthesized for desalination purposes. Membrane performance in this work is relatively not much different on account of both the selectivity and the production quantity. However, the performance of this membrane is far below that of cobalt silica membranes.

12 Conclusions

In this study, the TEOS-MTES silica membranes were prepared with variations in the TEOS-MTES composition of 100-0, 90-10, 75-25, 50-50, 25-75, 10-90, and 0-100 through the sol–gel process and calcined at 350 and 500 °C. The hydrophobicity of the TEOS-MTES silica thin layer enhanced with increasing MTES content in the composition due to an increase in the C–H/Si–O–Si ratio and a decrease in the Si–OH/Si–O–Si ratio. Similarly, thermal stability increased with increasing MTES content. All silica xerogels exhibited microporous character, with pore volume and surface area decreasing with reduced TEOS content in the silica matrix. The composition of TEOS-MTES plays an essential role in determining the membrane's character and performance, salt rejection, and water fluxes. Higher TEOS content resulted in higher water flux. Conversely, higher MTES content generated higher salt rejection. All membranes provided good salt rejection with values up to 99%, especially those with high MTES content. Furthermore, this work paved the way for understanding the influence of hydrophilic and hydrophobic groups on silica structure and their relation to desalination performance.

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Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

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