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Hydrophobic Ceramic Membranes for Water Desalination

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Abstract: Hydrophilic ceramic membranes (tubular and planar) made of TiO 2 and Al 2 O 3 were efficiently modified with non-fluorinated hydrophobic grafting molecules. As a result of condensation reaction between hydroxyl groups on the membrane and reactive groups of modifiers, the hydrophobic surfaces were obtained. Ceramic materials were chemically modified using three various non-fluorinated grafting agents. In the present work, the influence of grafting time and type of grafting molecule on the modification efficiency was evaluated. The changes of physicochemical properties of obtained hydrophobic surfaces were determined by measuring the contact angle (CA), roughness (RMS), and surface free energy (SFE). The modified surfaces were characterized by contact angle in the range of 111–132°. Moreover, hydrophobic tubular membranes were utilized in air-gap membrane distillation to desalination of sodium chloride aqueous solutions. The observed permeate fluxes were in the range of 0.7–4.8 kg·m⁻²·h⁻¹ for tests with pure water. The values of permeate fluxes for membranes in contact with NaCl solutions were smaller, within the range of 0.4–2.8 kg·m⁻²·h⁻¹. The retention of NaCl in AGMD process using hydrophobized ceramic membranes was close to unity for all investigated membranes.

Keywords: ceramic membranes; non-fluorinated alkylsilanes; air-gap membrane distillation

1. Introduction

Membrane distillation (MD) is an emerging non-isothermal membrane separation process, being one of the promising techniques for the desalination of highly saline waters [1–7]. Contrary to pressure-driven techniques, the driving force in the membrane distillation process is related to the difference in chemical potential (generated by difference of temperatures) between the two sides of the hydrophobic membrane [8–10]. The non-wetted porous hydrophobic membranes are required for an efficient process realization. There are various MD modes utilized, for example, sweep gas membrane distillation (SGMD), direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), vacuum membrane distillation (VMD) [1,5,9,11]. MD can be used in different applications such as waste water treatment, desalination, and food processing [1,3,5,11–19]. In all configurations, the liquid–vapor equilibrium is the determining factor yielding to the selectivity of the MD processes. The mass transfer in MD follows three subsequent steps: liquid–vapor phase transition at the membrane pores entrance on feed side; transfer of vapors through the pores of the membrane; and condensation of vapors on the permeate side of the membrane [1–7].

Despite the fact that, in the MD process, high pressure is not required and the process offers a very promising performance for both the stand-alone and the desalination process, full-scale commercialization of MD still copes with various problems. These difficulties are related to the lack of
suitable and effective module design, proper membranes, as well as intensive energy consumption (in cases when waste heat, solar, or different alternative energy sources are not utilized). In the presented article, the authors address the issues related to the lack of suitable membranes. The major requirements for the membrane features are related to hydrophobic character and porous structure [20]. During the MD process only vapors of solvent (water) are allowed to pass across the membrane. Concerning scientific literature focused on MD application, it is possible to find application of commercially-available hollow fiber or flat-sheet microfiltration membranes [16,21–29]. The utilization of these membranes in MD is associated with their hydrophobic properties, decent porosity, as well as adequate pore sizes. Nevertheless, these membranes are not the perfectly-designed and dedicated to membrane distillation, therefore they suffer from wetting problems as well as low permeability and short life span [9,21–26,30].

To design and form hydrophobic surfaces with certain properties, two approaches can be selected. One possibility is the creation of a rough surface with a structure responsible for its hydrophobicity. By generating heterogeneity on the surface, it is possible to form highly hydrophobic surfaces due to generation of pillars and the presence of air pockets on the surface. The other way is utilization of chemical modification applying grafting agent materials possessing the low surface free energy [31,32]. Up till now, a number of methods have been developed to produce rough surfaces, like solidification of melted alkylketene dimer (AKD) [33], plasma polymerization/etching of polypropylene in the presence of polytetrafluoroethylene (PTFE) [34], microwave plasma-enhanced chemical vapor deposition (MWPE-CVD) of trimethylmethoxysilane (TMMOS) [35], anodic oxidation of aluminum [36], or an immersion of porous alumina gel films into boiling water [37]. Chemically attached coupling agents with low-surface-energy can be also efficiently used to turn the hydrophilic character materials to hydrophobic one [38–41]. Within that group of compounds, perfluoroalkylsilane (PFAS) molecules [42–45], hydrophobic polymers [46], as well as Grignard compounds [47,48] have been found to generate hydrophobic surfaces. The aforementioned grafting agents were efficiently modified by the chemical attachment to the ceramic support. Ceramic materials are characterized by high chemical, thermal, and mechanical stability; therefore, they are ideal materials for many applications in the chemical, biotechnological [49,50], food [51], and pharmaceutical industries [52,53], as well as in water and wastewater processing [40,41,49]. However, ceramic membranes are hydrophilic by nature. This material property limits the wider application of ceramic membranes. For that particular reason, the modification of membrane surface is required to change the surface character from hydrophilic to hydrophobic one. Considering the high effectiveness of the grafting process of ceramic materials and good performance in membrane-based separation techniques (e.g., vacuum pervaporation [42,43,54,55], vacuum membrane distillation [56], air-gap and direct membrane distillation [42,45], and organic solvent nanofiltration [47,48,57]) it should be pointed out that such modification also possessed disadvantages. Namely, a significant drawback is the presence of fluorine atoms in coupling agents. In the presented research fluorine-free modifiers were used for highly efficient hydrophobization process of ceramic membranes. Subsequently, the ceramic materials are tested in desalination process using membrane distillation (MD) technique. An important issue of the study was to evaluate the influence of the type of grafting agents and modification conditions on the membrane performance in MD.

2. Materials and Methods

2.1. Materials

Al₂O₃ (Pall Exekia, Bazet, France) and TiO₂ (TAMI Industries, Nyons, France) tubular ceramic membranes were used in the presented work. Alumina membranes possessed 100 nm pore size (MWCO ≈ 150 kDa), whereas titania ones were characterized by 100 kD (∼75 nm) molecular weight cut-off (MWCO). Both types of membranes were characterized by 10/5 mm of outer/inner diameters
The following grafting compounds were purchased from Linegal Chemicals (Poland): n-octyltrichlorosilane (C8Cl3); n-octyltrimethoxysilane (C8OEt3); and trichloro(octadecyl)silane (C18Cl3) were used. Chloroform (stabilized by 1% ethanol), acetone, ethanol, n-butanol, n-hexane, and glycerin were purchased from Avantor Performance Materials (Poland). All compounds and chemicals were used as received.

2.2. Experimental Protocol of Ceramic Membranes Modification

Grafting solutions (0.05 M) were prepared by dissolving an appropriate amount of alkylsilanes in chloroform (stabilized by 1% ethanol). The preparation steps and modification were performed under inert gas (argon) atmosphere to avoid polycondensation reaction [31–41]. Prior to grafting, the ceramic membranes (tubular and/or planar) were cleaned consecutively in ethanol, acetone, and distilled water for 10 min in each solvent and dried in an oven at 110 °C for 12 h. Subsequently, ceramic supports were modified by soaking samples in the grafting solution for a given period of time equal to 1.5 h followed by the second modification of 3 h what resulted in the total hydrophobization time equal to 4.5 h. Scheme of modification procedure is depicted in Figure 1. Subsequently, the grafting effectiveness was evaluated by the contact angle measurements in the case of planar membranes and by determination of water liquid entry pressure (LEPw) for tubular ceramics.

![Figure 1](right) ceramic membrane modification by alkylsilanes grafting agent and differences in hydrophobicity level (contact angle and water liquid entry pressure (LEPw)) before (left) and after (right) hydrophobization process.

2.3. Modified Membrane Characterization—Analytical Methods

Contact Angle (CA) and Surface Free Energy (SFE): Static and dynamic contact angles (CA) measurements were performed at room temperature using the goniometer PG-X (FibroSystem AB) and deionized water (18 MΩ cm) and glycerin as testing liquids. CAs were determined for pristine and grafted membranes, based on sessile drop (static CA) and the tilting plate (dynamic CA) methods described elsewhere [44,45]. The apparent CA values were calculated by ImageJ software (ImageJ, NIH—freeware version), with an accuracy of ±2°. Additionally, a contact goniometric analysis was implemented for surface free energy (SFE) assessment for planar ceramic membranes. SFE was
calculated based on the Owens–Wendt method [58]. The results are presented as an average value obtained from 20 to 30 measurements (average accuracy of ±5%).

Atomic force microscopy (AFM): This technique was used for surface analysis (topography and phase analysis) of planar membranes (NanoScope MultiMode SPM System and NanoScope IIIa Quadrex controller—Veeco, Digital Instrument, Saint Ives, Cambridgeshire, UK). Tip scanning mode was applied for surface roughness analysis. Ambient temperature conditions were kept during all experiments. The root mean squared (RMS) roughness was used as a parameter describing heterogeneity of the samples. Scan size areas were equal to 5 × 5 µm. All samples were analyzed at least five times and an average value of RMS was calculated (accuracy ±5%).

Liquid entry pressure (LEPw): The grafting effectiveness of tubular membranes was assessed by liquid entry pressure determination (LEPw)—Equation (1). LEPw is a pressure value at which liquid penetrates across open pores of the membrane and is transported through the hydrophobic layer on the permeate side [11,23,42,59]. According to the Laplace–Young equation (Equation (1)), it can be noticed that LEPw value refer to the surface tension (γL), contact angle (θef) on membrane surface, pore radius (r), and tortuosity factor (B).

\[
\text{LEP}_w = -B \frac{2\gamma_L}{r} \cos \theta_{ef}
\]  

(1)

The LEPw measurements were realized using a laboratory experimental rig presented in detail elsewhere [42]. LEPw values were determined for all tubular membrane samples, prior to the membrane characterization in membrane distillation process. During the LEP measurements, the time interval between each pressure step was equal to 60 min.

2.4. Air-Gap Membrane Distillation (AGMD)

Membranes efficiency was evaluated in desalination process using air-gap membrane distillation (AGMD) technique and experimental rig presented in Figure 2. The AGMD experimental setup and the detailed experimental protocol are described elsewhere [42,45]. AGMD process was realized at temperate of feed equal to T_f = 90 °C and permeate equal to T_p = 5 °C. The air gap width was equal to 5 mm (Figure 2). Measurements were realized for pure water and for the following feed concentrations of NaCl aqueous solutions: 0.25, 0.5, 0.75, and 1.0 M. Rejection coefficient of sodium chloride (Equation (2)) was controlled by ion chromatography (Dionex DX-100 Ion Chromatograph).

\[
R_{NaCl} = \left(1 - \frac{C_p}{C_f}\right) \times 100 \text{ (\%)}
\]

(2)

where C_p and C_f stand for the NaCl concentration in permeate and feed solution, respectively.

![Figure 2](image-url)

Figure 2. Scheme of a setup used in AGMD experiments (1—thermostated feed tank; 2 and 6—pump; 3—AGMD thermostated membrane module with air gap = 5 mm; 4—measuring cylinder; 5—balance; 7—cooling system).
3. Results and Discussion

3.1. Pristine Ceramic Membranes

Planar unmodified TiO$_2$ 100 kD membrane possessed hydrophilic character with a surface contact angle value equal to $40 \pm 2^\circ$ and total surface free energy equal to $140 \pm 5$ mN·m$^{-1}$ (polar part $44.8 \pm 1.4$ mN·m$^{-1}$; dispersive part $95.2 \pm 3.1$ mN·m$^{-1}$). Roughness of unmodified ceramic sample expressed by RMS was equal to $60.5 \pm 5.1$ nm. Pristine tubular membranes TiO$_2$ 75 nm and Al$_2$O$_3$ 100 nm were characterized by LEPw equal to 0 bar.

3.2. Effectiveness of Membrane Hydrophobization

The hydrophilic character of planar membrane was turned to hydrophobic one with high efficiency. As a result of hydrophobization, the changes in morphology and physicochemistry of the membrane surface are clearly noticeable (Table 1). All membrane samples possessed contact angle values higher than $90^\circ$. The significant increase of water contact angle confirms the formation of the hydrophobic surface. Based on results presented in Table 1, it can be concluded that modification conditions (time and type of grafting agent) have an essential impact on the resulting hydrophobicity level. The highest value of CA was found for samples modified by C18Cl$_3$ molecules, i.e., the molecules with the longest hydrocarbon chain (~2.3 nm). Moreover, comparing ceramics grafted by silanes possessing the same length of alkyl chains, higher CA value was found for C8Cl$_3$ than for C8OEt$_3$. This observation is related to the bond dissociation energy which is equal to 489.5 kJ mol$^{-1}$ and 510.5 kJ mol$^{-1}$ for Si–Cl and Si–OEt, respectively [60]. Similar relation was found for ceramic powders (TiO$_2$ and ZrO$_2$) modified by non-fluorinated compounds possessing various reactive groups (e.g., methoxy, ethoxy, and chlorine atoms) [44]. The grafting process affects physicochemistry of ceramics, which was proved by the resulting reduction of surface free energy (SFE) value. It was found that polar component ($\gamma_p$) in overall SFE is very small (Table 1). Small contribution of the polar part compared to the dispersive component ($\gamma_d$) of SFE is characteristic for hydrophobic and highly hydrophobic materials [42,45,58,61]. Hydrophobization process also influences the surface roughness. The roughness parameter is reduced after grafting and it decreased even more after the extension of grafting duration. Silanization generated smoother surfaces with higher level of hydrophobicity. Namely, the smoothest surface possessing simultaneously the lowest value of overall SFE was achieved for samples modified by C18Cl$_3$ during 4.5 h.

Table 1. Characterization of modified planar ceramic membrane.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Pristine</th>
<th>Ti-C8OEt$_3$</th>
<th>Ti-C8Cl$_3$</th>
<th>Ti-C18Cl$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact angle (CA), deg</td>
<td>40 ± 2</td>
<td>111 ± 2</td>
<td>113 ± 2</td>
<td>120 ± 2</td>
</tr>
<tr>
<td>SFE, mN·m$^{-1}$</td>
<td>140 ± 5</td>
<td>62.5 ± 2.7</td>
<td>53.6 ± 2.3</td>
<td>43.7 ± 1.9</td>
</tr>
<tr>
<td>Polar part of SFE ($\gamma_p$), mN·m$^{-1}$</td>
<td>44.8 ± 1.4</td>
<td>13.3 ± 0.6</td>
<td>11.4 ± 0.5</td>
<td>9.3 ± 0.4</td>
</tr>
<tr>
<td>Dispersive part of SFE ($\gamma_d$), mN·m$^{-1}$</td>
<td>95.2 ± 3.1</td>
<td>49.2 ± 2.2</td>
<td>42.2 ± 1.8</td>
<td>34.4 ± 1.5</td>
</tr>
<tr>
<td>RMS, nm</td>
<td>60.5 ± 5.1</td>
<td>50.9 ± 2.0</td>
<td>45.2 ± 1.8</td>
<td>39.6 ± 1.6</td>
</tr>
</tbody>
</table>

The efficiency of tubular membranes modification was assessed by determining LEPw values for alumina and titania membranes after 1.5 h and 4.5 h of modification (Figure 3). A substantial influence of grafting time on the LEPw values, especially for samples grafted by C18Cl$_3$ molecules (Figure 3) was observed. After 1.5 h of hydrophobization LEPw value equal to 1 bar for alumina and titania membranes were observed. Longer exposure of membranes to the grafting agent resulted
in the increase of LEPw values to 7 bar and 4 bar for Al₂O₃ and TiO₂ membrane, respectively. The highlighted differences between ceramics can be linked to the membrane material and availability of different amounts of hydroxyl groups available to generate covalent bonds between ceramic surface and grafting coupling agent. Concerning the material properties of ceramics and data presented elsewhere [44], it was found that alumina is richer in hydroxyl groups comparing with titania. For this reason, higher value of LEPw for Al₂O₃ has been noticed. A slightly higher value of LEPw for C8OEt₃ than C8Cl₃ after a longer modification time might be related to the presence of hydroxyl groups still available after the first grafting process that were not used for covalent bonding.

![LEPw evolution with grafting time for alumina and titania ceramic materials grafted with various alkylsilanes.](image)

**Figure 3.** LEPw evolution with grafting time for alumina and titania ceramic materials grafted with various alkylsilanes.

### 3.3. Air-Gap Membrane Distillation—Separation Efficiency of Modified Ceramic Membranes

Prior to desalination process of NaCl solutions, membranes were tested in contact with pure water as a feed solution to evaluate the nominal value of water permeate flux (Figure 4). The fluxes in contact with pure water were the higher that those for NaCl solutions. Membrane grafted by C8COEt₃ possessed the highest value of permeate flux (Figure 4). On the other hand, the less permeable was the membrane grafted by molecules having the longest alkyl chains. The permeate flux through the grafted ceramic membranes decreased with increasing salt concentration in the feed (Figure 4). This behavior was caused by the fact that, in membrane distillation of NaCl solutions, only vapors of water are transported across the hydrophobic porous structure of the membrane and with higher concentration of non-volatile compounds in the feed (sodium chloride) a decline of the flux is observed. For this reason, with increase of salt concentration a diminution of driving can be noticed, according to the Raoult’s law.
The salt retention ($R_{NaCl}$) during the membrane distillation process was calculated according to Equation (2). The obtained values of $R_{NaCl}$ were very high, close to 100% (Table 2). A small effect of grafting time on the $R_{NaCl}$ values was observed. On the other hand, no influence of membrane materials on their selective properties was noticed. The observed small alteration in $R_{NaCl}$ corresponds to the separation properties of applied membranes.

Figure 4. Transport properties of modified ceramic membranes by (A) C8Cl3; (B) C8OEt3; and (C) C18Cl3, molecules in AGMD process used for desalination. $T_f = 90 \, ^\circ C$; $T_p = 5 \, ^\circ C$, $\Delta p = 688 \, mbar$.

After a shorter grafting (1.5 h), the alumina membrane modified by C8OEt3 molecules showed the highest value of permeate flux 4.84 kg m$^{-2}$ h$^{-1}$ which corresponded to the lowest value of measured $\Delta$Pw (Figure 4B). On the other hand, a membrane sample hydrophobized by molecules with longer alkyl chain (C18Cl3) showed the poorest transport properties. This can be attributed to the presence of alkyl chain in a tangled environment and/or partially located in pores [56].

The Al-C18Cl3 membranes produced the lowest value of permeate flux. This observation can be explain by a higher effectiveness of grafting comparing molecules with reactive groups of chlorine atoms and ethoxyl groups. As mentioned above, molecules with chlorine atoms are characterized by the highest ability to generate covalent bonds due to the lower value of energy bonds [60]. The membrane material as well as time of modification process affected the transport properties. Generally, membranes made from alumina possessed a slightly higher value of permeate flux due to slightly bigger pores (100 nm) in comparison with titania ones (≈75 nm). The observed reduction of permeate fluxes (Figure 4) as well as $\Delta$Pw values (Figure 3) with extended grafting time contributed to formation of a smoother surface (Table 1) showing better water-proof character. Summarizing the fabricated hydrophobic membranes possess good transport properties in AGMD compared with literature data [40,42,62,63]. Furthermore, the observed values of permeate fluxes are higher than for ceramic membranes tested in DCMD. This is related to the benefit of AGMD, namely the reduction of conduction heat losses. In AGMD, permeate is condensed on a chilled surface rather than directly in the chilled permeate. Nevertheless, the achieved permeate fluxes for ceramic membranes are smaller than for polymeric one [64].

Retention coefficient of salt ($R_{NaCl}$) Equation (2) is a very important factor determining efficiency of membrane distillation process. $R_{NaCl}$ corresponds to the separation properties of applied membranes. The salt retention ($R_{NaCl}$) during the membrane distillation process was calculated according to Equation (2). The obtained values of $R_{NaCl}$ were very high, close to 100% (Table 2). A small effect
of grafting time on the $R_{NaCl}$ values was observed. On the other hand, no influence of membrane materials on their selective properties was noticed. The observed small alteration in $R_{NaCl}$ values can be explained by marginal differences in physiochemistry of the membrane (CA, LEPw, and RMS). Nevertheless, the value of $R_{NaCl}$ was high, proving that no wetting of the membranes was observed.

### Table 2. Range of retention coefficient (%) of NaCl in AGMD process.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>1.5 h Modification</th>
<th>4.5 h Modification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-C8Cl3</td>
<td>98.0–98.3</td>
<td>99.5–99.6</td>
</tr>
<tr>
<td>Ti-C8OEt3</td>
<td>98.3–98.5</td>
<td>99.6–99.7</td>
</tr>
<tr>
<td>Ti-C18Cl3</td>
<td>98.0–98.4</td>
<td>99.2–99.6</td>
</tr>
<tr>
<td>Al-C8Cl3</td>
<td>98.1–98.3</td>
<td>99.0–99.5</td>
</tr>
<tr>
<td>Al-C8OEt3</td>
<td>98.0–98.3</td>
<td>99.0–99.3</td>
</tr>
<tr>
<td>Al-C18Cl3</td>
<td>98.0–98.2</td>
<td>99.0–99.3</td>
</tr>
</tbody>
</table>

### 4. Conclusions

The surface character of $\text{Al}_2\text{O}_3$ and TiO$_2$ ceramic membranes (tubular and planar) was changed from a hydrophilic to hydrophobic one by chemical modification with silane grafting agents possessing various structures (length of alkyl chain and type of reactive groups). After modification, highly hydrophobic surfaces were fabricated.

The length of hydrophobic PFAS molecule has a significant impact on the hydrophobicity level. Much higher values of CA and LEPw were observed for planar and tubular membranes grafted by C18 molecules comparing with C8 ones.

Hydrophobization process changed the physicochemical properties of ceramic membranes expressed by their roughness, surface free energy (polar and dispersive component), and hydrophobicity level.

The obtained hydrophobic tubular ceramic membranes were used in membrane separation process—air gap membrane distillation. In AGMD, process impact of concentration of NaCl in the feed, grafting time, as well as type of membrane materials on the transport properties was observed and discussed in detail. Higher values of permeate flux were observed for alumina membranes than for titania ones, which resulted from higher LEPw values for grafted alumina. The retention coefficient of NaCl in AGMD process using hydrophobized ceramic membranes was over 98% for all investigated membranes.

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### Author Contributions:
Joanna Kujawa and Wojciech Kujawski conceived and designed the experiments; Joanna Kujawa and Sophie Cerneaux performed experiments and collaborated with the data analysis; Katarzyna Knozowska collaborated with interpretation of the experimental data (contact angle, membrane distillation), assisted with critical corrections in the manuscript drafting, and prepared the drawings; Joanna Kujawa and Wojciech Kujawski participated in the analysis and interpretation of the experimental data, cooperated with the drafting and correction of the final version of the manuscript.

### Conflicts of Interest:
The authors declare no conflict of interest.

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