

Article



Eco-Friendly Superhydrophobic Modification of Low-Cost Multi-Layer Composite Mullite Base Tubular Ceramic Membrane for Water Desalination

Javad Zare¹, Mohsen Abbasi^{1,*}, Seyed Abdollatif Hashemifard¹, Nadir Dizge², Mahdieh Dibaj³ and Mohammad Akrami^{3,*}

- ¹ Sustainable Membrane Technology Research Group, Department of Chemical Engineering, Persian Gulf University, Bushehr 75169, Iran; javadezare1994@gmail.com (J.Z.); salhashemifard@pgu.ac.ir (S.A.H.)
- ² Department of Environmental Engineering, Mersin University, 33343 Mersin, Turkey; ndizge@mersin.edu.tr
- ³ Department of Engineering, University of Exeter, Exeter EX4 4QF, UK; m.dibaj3@exeter.ac.uk
- * Correspondence: m.abbasi@pgu.ac.ir (M.A.); m.akrami@exeter.ac.uk (M.A.)

Abstract: This study aimed to investigate and develop a cost-effective and superhydrophobic ceramic membrane for direct contact membrane distillation (DCMD) applications. Two types of mullitebased composite membranes were prepared via extrusion and sintering techniques. To create a small and narrow pore diameter distribution on the membrane surface, the dip-coating technique with 1 µm alumina was employed. The hexadecyltrimethoxysilane eco-friendly grafting agent was adopted to modify low-cost multilayer mullite-based composite membranes, transforming them from hydrophilic to superhydrophobic. The prepared membranes were characterized via field emission scanning electron microscopy (FESEM), energy-dispersive spectrometry (EDS), Fourier Transform Infrared Spectroscopy (FT-IR), X-ray diffraction (XRD), liquid entire pressure (LEP), contact angle, atomic force microscopy (AFM), porosity, and membrane permeability. The results of the prepared membranes validate the appropriateness of the material for membrane distillation applications. The optimized membrane, with a contact angle of 160° and LEP = 1.5 bar, was tested under DCMD using a 3.5 wt.% sodium chloride (NaCl) synthetic solution and Persian Gulf seawater as a feed. Based on the acquired results, an average permeate flux of $3.15 \text{ kg/(m^2 \cdot h)}$ and salt rejection (R%) of 99.62%were found for the 3.5 wt.% NaCl solution. Moreover, seawater desalination showed an average permeate flux of 2.37 kg/($m^2 \cdot h$) and salt rejection of 99.81% for a 20-h test without any pore wetting. Membrane distillation with a hydrophobic membrane decreased the turbidity of seawater by 93.13%.

Keywords: ceramic membrane; membrane distillation (MD); direct contact membrane distillation (DCMD); seawater desalination

1. Introduction

The development of both rural and urban areas, coupled with an increasing population, highlights the crucial need for high-quality water that can be utilized not only for drinking but also for various other beneficial purposes. Over the past few decades, water pollution has emerged as a significant global concern due to industrial growth [1,2]. The increased need for clean water is a result of both population expansion and industrial development. Global climate change and heightened levels of pollution have made the shortage of fresh water one of the major obstacles faced in the contemporary age. Seawater desalination is commonly acknowledged as a vital approach for enhancing water supplies and tackling the growing demand for freshwater, thus alleviating water scarcity [3]. As a result, brackish water desalination technologies have become more important for drinking water production [2]. Conventional water desalination technologies have their drawbacks. For example, using reverse osmosis (RO) in low-income countries can be financially burdensome, and working under pressure causes significant membrane fouling [4]. Furthermore,



Citation: Zare, J.; Abbasi, M.; Hashemifard, S.A.; Dizge, N.; Dibaj, M.; Akrami, M. Eco-Friendly Superhydrophobic Modification of Low-Cost Multi-Layer Composite Mullite Base Tubular Ceramic Membrane for Water Desalination. *Water* 2024, *16*, 1593. https:// doi.org/10.3390/w16111593

Academic Editors: Noemi Melián Martel and Baltasar Peñate Suárez

Received: 19 April 2024 Revised: 27 May 2024 Accepted: 29 May 2024 Published: 1 June 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). reverse osmosis (RO) plants exhibit a greater reliance on energy sources like oil and gas, which consequently makes them susceptible to fluctuations in their prices. This is primarily attributed to the high-pressure requirements associated with RO technology. In contrast, emerging technologies, like membrane distillation, offer a promising alternative as they are less reliant on traditional energy sources [2,3]. Recently, the membrane distillation process has been explored as a viable alternative in the literature [5]. Membrane distillation is gaining popularity as a water supply method due to its zero discharge and high water recovery rate, reaching up to 80% for seawater [6]. MD is a separation technique that relies on the vapor pressure difference of volatile substances passing through the pores of a hydrophobic membrane [7]. The MD process is a unique combination of thermal and membrane techniques, where the liquid feed is transformed into vapor and conveyed through hydrophobic membrane pores [7,8]. In addition to wastewater treatment, the MD process can be employed to produce fresh water, remove heavy metals, recover salt from high-concentration aqueous solutions, address radioactive pollution, and facilitate the removal of produced ethanol in the food industry [8]. The remarkable features of the MD process include high-purity products, compact volume, performance at low pressure (about 1 bar), low sensitivity to concentration polarization, and most importantly, distillation below boiling point (40–80 °C), which helps to reduce costs and energy consumption and also demonstrate a higher level of resistance to scaling in comparison to the RO process [9-12]. The MD process, despite being driven by thermal energy, has the capability of utilizing sustainable energy sources such as solar power, geothermal energy, and hot industrial waste streams in order to reduce energy consumption [3,13]. Dow et al. [14] used waste heat in the DCMD process as an energy source and achieved a permeate flux of 3 L/m^2 h. Iqbal et al. used solar energy for a DCMD system, which could produce up to 14.33 m³ of freshwater per day with a water production cost of $0.64/m^3$. Various MD process configurations, such as direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), swept gas membrane distillation (SGMD), and vacuum membrane distillation (VMD), are commonly used for separation based on merit, and relevant properties are considered [15]. The DCMD process stands out as the most extensively employed configuration among these setups due to its uncomplicated design and process, which eliminates the need for supplementary equipment like vacuum pumps or condensers. This particular configuration is extensively utilized in the process of desalination, the reclamation of water from textile wastewater, and the concentration of aqueous solutions. Wang et al. [16] utilized DCMD for water desalination and reported satisfactory permeate flux $(1.67-8.33 \text{ L/m}^2 \cdot h)$ and salt rejection. However, the full implementation of DCMD in the industry has not yet been realized due to significant obstacles to commercial adoption that have been extensively examined in previous studies. These barriers include membrane and module design challenges, membrane pore wetting issues, low permeate flow rate, flux decay, as well as uncertain energy and economic costs [17–20]. In this study, the focus has been on this configuration and economical materials for the preparation of this technology on a pilot scale.

The membranes used in the MD process are usually made from a variety of materials, such as organic (polymeric), inorganic (ceramic), and composite/hybrid (organic and inorganic) materials. Undoubtedly, the utilization of polymeric materials in this technique is unquestionable, primarily owing to their intrinsic hydrophobic nature, extensive accessibility in the market, and cost-effectiveness. Nevertheless, polymer membranes exhibit certain drawbacks, including limited mechanical, chemical, and temperature stability. For instance, abrupt heat-induced alterations may occur during the MD process at approximately 60 °C. As a result, the polymer membrane is unlikely to endure for an extended period and typically deteriorates at this temperature [21,22]. Their industrial application is a matter of great concern considering these issues, while none of them currently meet the basic requirements for an economically viable DCMD process [23]. Due to these shortcomings, ceramic membranes are increasingly preferred because of their resilience to heat-induced changes, even when operating at temperatures above 1000 °C [24]. The focus of this study

is on ceramic membranes because of their unique qualities, such as their low density, low thermal conductivity, exceptional stability at high temperatures and pressures, and impressive durability resulting from their high hardness and strength [25]. Despite the limitations posed by the high cost of raw materials and sintering temperature, the utilization of ceramic membranes has been successfully addressed by researchers through the implementation of cost-effective alternatives like kaolin [26–29]. For the required energy, the use of low-cost, renewable energy sources, including geothermal energy, solar energy, and waste heat from industrial systems was suggested [30–33]. The hydrophilic nature of ceramic membranes poses another hindrance to their utilization in the MD process. To overcome these challenges, researchers have suggested some hydrophobization solutions, such as physical or chemical mechanisms involving the addition of particles that provide roughness or coating, or by linking agents with long alkyl chains, respectively [34].

Hydrophobic ceramic membranes are commonly produced using fluorinated silanes, which are widely acknowledged in the literature as the preferred modifying agents for MD applications due to their ability to meet the necessary criteria. However, it is important to note that while fluorinated silanes are popular, they are not the sole modifying agents employed in this context [35]. Song et al. [36] modified their α -alumina support with fluoroalkylsilane (FAS) and the result was promising for application in the AGMD process. Their experimental reports have presented promising results, with a superhydrophobic membrane surface exhibiting a contact angle higher than 150°, a permeate flux of 12.68 kg/m²·h, and a salt rejection rate of 98.5%. Other experimental studies that use FAS have also shown similar results [37–40].

Considering the adverse effects of using fluorinated hydrophobized agents on human health and the environment, as well as their durability and potential long-life degradation in the environment, greener solutions for water hydrophobization were investigated [41-43]. It is possible to create hydrophobic ceramic membranes using a fluorine-free modifying chemical like hexadecyltrimethoxysilane because it is less expensive and simpler to store than FAS. Chen et al. [13] used a fluorine-free agent by grafting a method to hydrophobize the alumina membrane (superhydrophobic contact angle $> 150^{\circ}$). The performance result was favorable, with a durability time of more than 1000 min and a permeate flux of $30 \text{ kg/m}^2 \cdot \text{h}$. Twibi et al. [5] used Saudi red clay to produce a membrane, which was then modified by the grafting method using tetraethyl orthosilicate (TEOS) for VMD application. Their results showed a contact angle of 95.7° and permeation flux of 13.1 kg/m² h with a salt rejection of more than 98%. The MD process heavily relies on the size of the pores within a porous membrane. It has been determined that raising the porosity and average pore diameter will increase the permeate flux. In order to avoid the issue of membrane wetting during the MD process, it is crucial to maintain an operating pressure that is below the liquid entry pressure (LEP). To enhance the permeate flux and achieve improved performance in the MD process, it is essential for the porous membrane to possess a moderately large pore diameter. Additionally, the membrane should exhibit small pore diameters and a narrow distribution of pore diameters to minimize the likelihood of membrane wetting [44].

The utilization of kaolin and calcium carbonate in conjunction with the coating technique for the MD process is quite limited, resulting in a scarcity of available data on these materials. Consequently, when comparing these ceramic materials to the extensively employed PVDF polymer material in MD systems, the number of studies conducted on them is incomparable. Nevertheless, researchers continue to dedicate their efforts towards the research and development of PVDF for MD systems. As a result, there is a significant amount of work and development required to achieve higher fluxes in the field of MD, particularly in relation to the economical ceramic materials utilized in this study. For this purpose, a multilayer membrane has been introduced to control the pore size of the membrane. The objective of this research is to overcome the high cost of raw materials for ceramic membrane fabrication by utilizing cost-effective materials such as kaoline and by modifying a green composite multi-layer ceramic membrane for the membrane distillation process. In order to enhance the level of hydrophobicity with hexadecyltrimethoxysilane and its durability over time, the alumina slurry was coated with 1-micron particles using the dip coating method for the first time before treatment. The effectiveness of the prepared membranes was tested via direct contact membrane distillation for the desalination of synthetic brine water (3.5 wt% NaCl) and Persian Gulf seawater.

2. Materials and Methods

2.1. Raw Materials

The salt used in this research was obtained from Merck, Darmstadt, Germany, to prepare the salt water (3.5 wt.%). Kaolin powder was supplied from Zaminkav company, Tehran, Iran. Table 1 illustrates the chemical composition of kaolin. Calcium carbonate powder was used to prepare the MD support membrane, and alpha-alumina powder with a mean particle size of 1 µm and 99.6% purity was supplied by Semnan Mine, Iran, to prepare the intermediate layer. The price of natural kaolin and calcium carbonate powder from Iranian mines was less than 0.1 \$/kg (world price: 0.2 \$/kg), and alumina powder with a purity of 99.6% was 2.08 \$/kg (world price: ~2 \$/kg). Arabic gum (light yellow, moisture 9.7% by weight), used as a binder, was supplied by Merck, Germany. Hexade-cyltrimethoxysilane 85% (Sigma Aldrich, Taufkirchen, Germany) and 99.7% ethanol (Merck, Darmstadt, Germany) were used to modify the surface of the prepared ceramic membranes.

Table 1. Chemical composition of kaolin (wt.%).

Chemical Composition	Value	
SiO ₂	61.62	
TiO ₂	0.40	
Al_2O_3	24–25	
Fe ₂ O ₃	0.45-0.65	
K ₂ O	0.40	
Na ₂ O	0.50	
L.O.I	9.5–10	
L.U.I	9.5–10	

2.2. Brine Water Preparation

For the operational tests of desalination via membrane distillation, synthetic salt water (3.5 wt.%) and Persian Gulf seawater, whose characteristics are listed in Table 2, were utilized.

Table 2. Specification of seawater.

Parameter	Value
EC (mS/cm)	60 ± 0.1
TDS (ppm)	$42,000\pm95$
pH	8.8 ± 0.1
Salinity (PSU)	40.5 ± 0.2
Turbidity (NTU)	11.65 ± 0.1

2.3. Procedure of Ceramic Support Membrane Fabrication

To fabricate the base ceramic membrane, kaolin and calcium carbonate were prepared in ratios of 0:100 (M1) and 70:30 (M2) to create membranes with two different porosities, as CaCO₃ could increase the porosity using the extrusion and sintering method [45]. After preparing the ceramic paste, it was extruded and cut into a 280 mm length membrane. The membrane that was prepared had an inner diameter of 10 mm and an outer diameter of 14 mm. The membrane support was sintered in a furnace (1200 °C Mini Lab Electric, T-Long, Guangzhou, China) according to the temperature steps used in previous studies, up to 1250 °C, and was cooled at room temperature for the preparation of the next steps, as shown in Figure 1 [46].



Figure 1. Thermal temperature applied for sintering MD membrane support.

2.4. Intermediate Layer

The immersion method was utilized to coat the middle layer on the prepared support. The dispersion process involved dispersing 27.7 g of an alumina suspension, which had an average particle size of 1 μ m in 150 mL of distilled water. This dispersion was achieved by subjecting the mixture to an ultrasonic bath treatment for a duration of 15 min at a temperature of 25 °C. In a separate container, a solution of Arabic gum (5.5 g) was prepared by dissolving it in 100 mL of distilled water at a temperature of 50 °C for a duration of 6 h. The resulting solution was then subjected to dispersion using a homogenizer, followed by sonication for 15 min to achieve a uniform and consistent dispersion. Finally, the alumina slurry was slowly added to the container and the membrane was immersed in this solution for 10 s. After layering, the wet membrane was dried at 80 °C for 4 h. In the final step, the layered membrane was sintered in the furnace according to Figure 1, with a final temperature step up to 1150 °C [46].

2.5. Preparation of the Hydrophobic Membrane

The modification agent hexadecyltrimethoxysilane (HDTMS) is illustrated in Figure 2. The concentrated hexadecyltrimethoxysilane was mixed with ethanol to create the modifier solution, which had a concentration of 0.1 M. This mixing process was carried out at room temperature for a duration of 24 h. The untreated membranes and the membranes coated with alumina were submerged in the solution containing the modifier at a temperature of 35 °C for a duration of 2 h. The membranes were then washed with deionized water and then dried at 120 °C for 4 h. The membranes were stored at room temperature before characterization and water desalination. The ceramic membrane modification process included the hydrolysis of organosilane to impart hydrophobic properties. This chemical reaction produced a new compound containing multiple hydroxyl groups (-OH), which subsequently interacted with the hydroxyl groups present on the membrane's surface. As a result of this reaction, a hydrophobic grafted product was formed through dehydration. These sequential steps are illustrated in Figure 2 [15].



Figure 2. Chemical structure of modified agent (HDTMS) and scheme of surface modification with HDTMS [47].

2.6. Characterization of Fabricated Membranes

In order to determine the appropriate membrane characteristics and the suitability of the membrane characteristics for the membrane distillation process, the characteristics of the ceramic membrane were evaluated before and after surface modification. The morphology of the membranes' surface was evaluated using a field emission scanning electron microscope (FESEM, S-4800, Hitachi, Tokyo, Japan). The thickness of the layer was ascertained by analyzing the cross-sectional FESEM image of the membrane. The detection of HDTMS anchoring to hydroxyl sites was accomplished via fourier transform infrared spectroscopy (FTIR, Nicolet iN10, Thermo Scientific, Waltham, MA, USA), energy dispersive spectrometry (EDS), and X-ray diffraction (XRD). A surface angle analysis device was also used to analyze the hydrophobicity of the membranes' surface. The feasibility of the membranes under different operating pressures was also investigated using the liquid entry pressure (LEP) device. The laboratory setup, shown in Figure 3a, was used to determine the LEP of water. Using the Young–Laplace equation, the maximum pore size of the membranes could be predicted.

$$LEP = \frac{2\gamma_1}{\gamma_{max}} \cos(\theta) \tag{1}$$

where γ_1 represents the liquid surface tension, r_{max} is the maximum radius of the pores of the membrane and θ is the value of the membrane contact angle [48].

To investigate the permeability of the membranes, a microfiltration (MF) apparatus was used to assess the permeability of the membranes before and after modification. Figure 3b shows the permeability setup.



Figure 3. (a) Apparatus for measuring LEP and (b) schematic diagram of MF set up used for DCMD membrane permeability.

By employing Archimedes' experimental approach, it became possible to ascertain the porosity of membranes. This particular method entailed the measurement of various parameters such as length, inner and outer diameter, as well as the weight of each membrane subsequent to a 5 h drying period at a temperature of 150 °C. The membranes were then placed in water for a period of 12 h to allow the filling of pores with water. The wet membranes were reweighed after eliminating any surplus water present on their surface in order to ascertain their weight. The porosity of each membrane was calculated using the following Equations (2)–(4) [49,50].

$$\varepsilon = \frac{V_s}{V_t} \times 100 \tag{2}$$

$$V_{s} = \frac{M_{w} - M_{d}}{\rho_{w}}$$
(3)

$$\mathbf{V}_{\mathbf{t}} = \pi \mathbf{R}_0^2 \mathbf{L} - \pi \mathbf{R}_{\mathbf{i}}^2 \mathbf{L} \tag{4}$$

where ε , V_s , V_t stand for porosity, cavity volume, and total membrane volume, respectively. M_w is the wet membrane weight and M_d is the dry membrane weight. ρ_w is water density, R_i and R_o are the internal and external radius of the membrane, respectively.

The Guerout–Elford–Ferry Equation (5) was utilized to ascertain the average pore radius (r_m) of the MD membranes by employing distilled water and porosity [51].

$$r_{m} = \sqrt{\frac{(2.9 - 1.75\epsilon)8\mu LJ}{\epsilon TMP}}$$
(5)

The variables in the equation are defined as follows: ε represents the percentage of membrane porosity, L stands for the thickness of the membrane in meters, μ represents the viscosity of water at room temperature (specifically, 8.9×10^{-4} Pa·s), J represents the rate of water permeation per unit of time in cubic meters per second (m³s⁻¹), and transmembrane pressure (TMP) represents the operational pressure, which typically ranges from 0.5 to 2 bar.

2.7. Performance Test and Apparatus

The water desalination performance was tested with a fabricated hydrophobic membrane by direct contact membrane distillation (DCMD) with a feed flow rate of 3 L/h and a feed temperature of 68 °C. To determine membrane performance in two different salinity conditions, synthetic salt water and seawater were used for the experiments. Hot brine water was circulated as feed in the hot cycle and inside the membrane. Subsequently, the permeate underwent condensation into water via the membrane, which was then gathered in a distinct reservoir. To determine the permeate flux J (kg/(m²·h)), the collected water was weighed using a precision balance, and Equation (6) was employed.

$$J = \frac{M_d}{At}$$
(6)

where M_d is the weight of collected water, A is the active surface area of the membrane, and t is the measured time. Experiments were performed using the apparatus shown in Figure 4a,b. The experimental module and produced membrane are shown in Figure 4c–e.



Figure 4. (a) Schematic of the setup used in the DCMD experiments and (b) flow circulation in DCMD. Fabricated membrane and membrane module (c) raw membrane, (d) sintered membrane, and (e) tubular membrane module.

In the process of MD, water vapors passed through the pores of the membrane and condensed on the permeate side, effectively removing dissolved salts and non-volatile substances [52]. Permeate flux and salt removal were investigated using synthetic sodium chloride solution (3.5 wt.%) and Persian Gulf seawater (without any pre-treatment). The salt rejection (R) was obtained using Equation (7):

$$R\% = \frac{C_f - C_p}{C_f} \times 100 \tag{7}$$

where C_f and C_p represent salt concentration in the feed solution and permeate, respectively. A conductivity meter was used during the experiments to measure changes in salt concentration in the water. A commonly employed quantitative method to investigate the wettability state is contact angle measurement, which determines the extent to which a liquid spreads over a solid surface, thus indicating the surface's wetting properties [53]. The shape of the liquid droplet on the surface depends on the surface tension of the fluid and the characteristics of the solid surface. Contact angle measurements can be conducted using either a static or dynamic approach [54]. The static contact angle, or sessile drop technique, is the most commonly employed technique for measuring contact angles on smooth and uniform surfaces. It involves placing a droplet of the liquid onto the solid surface, allowing it to settle and fix the phase boundary. The contact angle between the solid–liquid interface is then captured using a camera [55,56]. This technique relies on Young's equation, which assumes that interfacial forces are thermodynamically stable.

3. Results and Discussion

3.1. Characterization of the Hydrophobic Ceramic Membranes

3.1.1. EDS Results

The EDS spectrum of the membranes was used to determine the elements of the fabricated membrane. The EDS spectrum in Figure 5 demonstrates the presence of C, O, Al, Ca, and Si in the M_2 membrane. By comparing before and after modification, the results indicated that the increase in Al and Si in the membrane was due to modification.



Figure 5. EDS spectrum of M2 (a) before and (b) after modification.

3.1.2. FESEM Results

The morphological change of the ceramic membrane (M2) was examined using FE-SEM before and after modification. Figure 6 illustrates a noticeable disparity in the surface morphology of the ceramic membrane before (Figure 6a) and after (Figure 6b) undergoing hydrophobic modification with HDTMS. The membrane pore size was significantly decreased through the process of hydrophobic modification. Figure 6d shows that the thin-coated layer could be seen as a bright layer on the internal and outer surface of the membrane in comparison with the unmodified one (Figure 6c). Therefore, further characterization was necessary to elucidate the process of modification. Figure 6e illustrates the pore fouling of the membrane due to the MD test. Subsequently, FTIR analysis was performed to investigate whether the modification occurred during the fabrication of the hydrophobic membrane.



Figure 6. FESEM image of tubular ceramic membrane surface roughness of M2 ceramic membrane (**a**) before and (**b**) after modification. Cross-section FESEM image of tubular M2 ceramic membrane (**c**) before, (**d**) after modification, and (**e**) after MD test.

3.1.3. FT-IR Results

FT-IR spectra were used to evaluate structural changes on the surfaces of the membranes (Figure 7). The comparison was performed between the unmodified M2 and modified M2 membranes and also between the M1 membrane and modified M1. Generally, the unmodified M2 membrane had a peak at 1010 cm⁻¹, corresponding to the C–O stretching bonds on the surface of the membrane [57,58]. Furthermore, a broad band in the spectra of the modified M2 membrane centered at 3315.5 cm⁻¹ was obviously attributed to the O–H bond, due to the hydroxyl group on the membrane surface [57,59]. The peaks at 2888 cm⁻¹ in the curves of the modified M1 and M2 membranes refer to a C–H bond [59,60]. The peak that appeared at 2211.95 corresponds to C≡C groups, which is related to the interaction between HDTMS and the M2 membrane. Compared to the unmodified curves, new peaks appeared at 1081.87 cm⁻¹, representing the asymmetric stretching of the Si–O–Si chain after modifying the surface with HDTMS [59]. It was determined that the modification occurred during the preparation of the hydrophobic membrane. The stretching vibration

absorption peak of Si–O appeared near 900 cm⁻¹ [61]. The peak at 786 cm⁻¹ in the spectra of the modified membrane is attributed to the Si–C stretching bond, which confirms the presence of a modification agent on the membrane surface [59]. Furthermore, the peak at 561.18 cm⁻¹ in the spectra of the modified membrane is attributed to the Si–O–Al stretching bond, which also confirms the presence of a modification agent on the membrane surface [62]. These results indicated that the wettability modification process was performed by a chemical agent (HDTMS) which was absorbed through the surface of the membrane by chemisorption. These results were consistent with the contact angle measurement of 160° and imaging characterization results (Figure 8).



Figure 7. FTIR spectrum of the ceramic membranes (M1: kaolin 100% and M2: kaoline 70% and CaCO₃ 30%) before and after modification.



Figure 8. Contact of the water droplet with the unmodified and modified membrane surface. (a) Before contact, (b) instantly after droplet contact with the surface of unmodified membrane, and (c) contact of the water droplet with the surface of HDTMS modified membrane.

3.1.4. XRD Results

X-ray diffraction (XRD) was conducted to analyze the phases that developed subsequent to the application of the coating onto the membrane, confirming the proper deposition of the hydrophobic hexadecyltrimethoxysilane layer. The ceramic membrane is associated with the phases of quartz, cristobalite, calcium carbonate, and mullite, as depicted in Figure 9. The peaks corresponding to the quartz phase are observable at approximately 21.54, 24.5, 26.5, 31.8, 37.42, and 61 degrees. Furthermore, the presence of the mullite structure is supported by the peaks observed at 30.9, 34.8, 38.9, and 61.98. The presence of the cristobalite phase is confirmed by the peaks observed at 21.98, 28.2, 31.31, 38.31, and 43.76 degrees. The identification of calcium carbonate is confirmed through the observation of peaks at 24.5, 29.6, 33.5, and 40.18 [1–4]. XRD analysis, in addition to revealing distinct peaks related to kaolin and calcium carbonate, had shown peaks related to alumina (Al_2O_3) and hexadecyltrimethoxysilane (SiO₂). The peaks at 20.02, 22.78, 24.58, 36.5, 39, 65.5, and 26.66 degrees exhibit significant intensity, indicating the presence of these compounds in the membrane structure [5–7]. From the observed peaks, it is clear that the hydrophobic compound, hexadecylteremethoxysilane, has effectively been applied as a coating on the membrane.



Figure 9. XRD of the ceramic membranes (M2: kaoline 70% and CaCO₃ 30%) after modification.

3.1.5. Contact Angle Results

The interaction between water droplets and the hydrophilic ceramic membrane (M2) was observed to examine the water contact angles, both before and after modification. Figure 8 illustrates that the contact angle of the original membrane decreases significantly from 30° to 0° in less than 0.5 s. This rapid decline could be attributed to the presence of –OH groups on the membrane's surface. However, following the hydrophobic modification, the membrane surface exhibited remarkable stability, with a contact angle greater than 158° when in contact with deionized water. This value surpassed the contact angle of 130° observed on the Al₂O₃ membrane grafted by FAS [63].

3.1.6. AFM Results

The three-dimensional AFM images in Figure 10 display the M1 and M2 surfaces in their initial conditions and after being coated with alumina suspension and modified with HDTMS. This analysis provided valuable information about the surface's behavior. The AFM images indicate that the intensity of the bright area grew following HDTMS grafting on both M1 and M2 surfaces. According to the literature, the lotus-like structure is represented by bright protrusions at the surface, and the pores are represented by dark depressions [64,65]. The surface roughness (R_a) of M1 increased from 3.485 to 4.228 nm after coating and grafting, while the R_a of M2 increased from 2.096 to 11.170 nm. This result indicated that surface modification had a better effect on the CaCO₃ composite support,



which could also be seen on the performance test due to the stronger bond that the surface alumina coating and HDTMS grafting created with the surface of the M2 membrane.

Figure 10. Three-dimension AFM images before and after modification of M1 and M2 membranes.

3.2. Effect of Modification on Water Permeation Flux

Figure 11 shows the comparison between the water flux of the original and modified ceramic membranes. In order to evaluate the separation properties of the membranes and also to calculate the average size of the membrane pores, the water flux of the microfiltration membranes was performed using deionized water at constant pressures of 1 to 4 bar. Membrane flux was measured for 30 min. The findings from the unmodified membrane demonstrated a direct correlation between water flux and pressure, indicating that the rise in pressure led to an increase in driving force, thereby enhancing the water flux. By examining the water flux of the modified membrane and the original membrane, it can be seen that the water flux of the modified membrane at a pressure of 1 bar is close to zero, and when the pressure is increased to 4 bar, this value reaches $1.4 \text{ kg/m}^2 \cdot \text{h}$, which is 0.22 of this value in the unmodified membrane. The low water flux of the modified membrane is proof of the 1-µm alumina-coated layer and the successful hydrophobicity of the membrane is surfaces, which is necessary for hydrophobic applications.



Figure 11. Comparison between water flux of original versus alumina-coated and HDTMS-treated ceramic membrane.

3.3. Modified Membrane Hydrophobicity Durability with Time

As seen in Figure 8b, when a drop was placed on the surface of the unmodified CaCO₃ and kaolin membrane, it was completely absorbed by the membrane surface and penetrated into it in less than half a second and did not show any resistance. This observation proves that both cheap kaolin and its composite with CaCO₃ membranes are extremely hydrophilic and do not show any resistance against water penetration. On the other hand, from Figure 12 it could be observed that the membrane coated with alumina and treated with HDTMS had a contact angle of 160° at the moment the water drop was placed on its surface. This case proves the change of the membrane's hydrophilic properties to superhydrophobic. By examining the recorded video and the dynamic contact angle of the water drop on the surface of the treated membrane, it could be seen that the drop remained on the surface for 60 min without changing the angle and did not show any decrease in the contact angle. With the passage of time, it was observed that the size of the droplet gradually decreased without changing the angle. The decrease in the size of the droplet on the membrane surface over time could be explained by the evaporation of the droplet from the membrane surface, due to the high temperature of the lamp in the contact angle analysis device.



Figure 12. Dynamic surface contact angle.

3.4. Liquid Entry Pressure

To ensure that the modified grafted membrane with HDTMS was suitable for distillation, the LEP test was conducted. The results showed that the modified membranes had three times more properties than the original ones. The final properties of both membranes are shown in Table 3. Interestingly, the maximum pore size calculated via the Young–Laplace equation gave almost the same value as the average pore size, i.e., ~0.40 μ m. This revealed that the pore size distribution was very sharp around ~0.40 μ m.

Property of M1	Before Modification	After Modification
Porosity (%)	42	36
Surface roughness (R_a) (nm)	3.485	4.228
Contact angle (°)	0	156
LEP (bar)	0	~1.5
Property of M2	Before Modification	After Modification
Porosity (%)	65	53
Surface roughness (R_a) (nm)	2.096	11.17
Contact angle (°)	0	160
LEP (bar)	0	~1.5
Average pore size (µm)	0.95	~0.40
Maximum pore size (µm)	0.95	~0.40

Table 3. Properties of M2 membrane before and after grafting.

3.5. Evaluation of Fabricated Membrane Performance in MD Application

The membranes that were prepared were subjected to salt water desalination experiments using DCMD in order to assess their suitability for use in the water desalination process. The investigation focused on water flux and salt rejection by utilizing a sodium chloride solution (3.5 wt.%) and seawater from the Persian Gulf. Throughout the experiment, all other operating conditions remained constant. Multiple tests were conducted to ensure that the hydrophobic modification of the membrane was done properly, and duplicating the MD performance test was undertaken to ensure the reliability and consistency of the results. DCMD tests were performed on the fabricated membranes, M1 (100% mullite support, alumina coated, and treated with HDTMS) and M2 (70% mullite, 30% CaCO₃ support, alumina coated, and treated with HDTMS), to remove NaCl from the synthetic salt water and seawater. The fabricated membrane was used in the DCMD process to obtain the permeate fluxes (J) and salt rejection (R%) percentages. The results for synthetic salt water can be seen in Figure 13a,b. The average distillation flux and salt rejection of the synthetic solution for the M1 membrane were $2.45 \text{ kg/(m^2 \cdot h)}$ and 99.051%, respectively, and for M2, an average J of $3.15 \text{ kg/(m}^2 \cdot \text{h})$ and R% of 99.62% were shown over a 5.5-h test. Comparisons between these two membranes led us to observe the presence of $CaCO_3$ in the support membrane (M2), which enhanced the porosity of the M2 membrane compared to M1. By comparing the results for M1 and M2, it was observed that M1 initially passed a higher flux, but after a period of time, the pores of the membrane became wet and clogged, and its permeability decreased over time. Another factor that affects flux reduction is membrane fouling [66,67]. In contrast to M1, M2, despite higher porosity due to the presence of $CaCO_3$ in its support structure and the micro-alumina layer on its surface, has reduced membrane wetting during the process and a more uniform flux reduction than M1. The reduction in the flux of both membranes was attributed to the reduction of surface tension at the system temperature, which is higher than the ambient temperature. However, the contact angle remained permanent, as shown in Figure 11, at room temperature. It is known that LEP is a function of both contact angle and surface tension. Therefore, this, in turn, led to a reduction in the membrane LEP, thereby wetting the membrane and causing a decline in the flux [2,59]. However, the trend of the flux was descending, but it approached a plateau, as shown in Figure 13. The results of salt removal compared to M1 also indicate the high durability of M2 in the membrane distillation process. Finally, the Persian Gulf

seawater was considered as the process feedwater for the operational investigation of the fabricated membrane under the DCMD process. The result of seawater desalination with an M2 membrane is shown in Figure 13c. The results revealed good desalination performance through the DCMD by the selected membrane over a 20-h test. An average permeate flux of 2.37 kg/m^2 ·h and salt rejection of the M2 membrane in this process was 99.81%, and it decreased the salinity of the sea water to 0 psu. In addition, after a 20-h sea water desalination test, the results indicated that the selected membrane (M2) had good stability over time.



Figure 13. (a) Permeate flux of M1- and M2-modified membranes using 3.5 wt.% NaCl, (b) salt rejection (R%) results for M1 and M2 membranes using a 3.5 wt.% NaCl, and (c) permeate flux and salt rejection (R%) results for M2 membrane using seawater.

The specification of permeate water after seawater desalination is shown in Table 4. DCMD had a great impact on feed seawater turbidity, and it decreased to 93.13%. The permeate flux of seawater showed a decrease through the DCMD process. The reason could be the fouling effect of seawater minerals and total dissolved solids (as mentioned in

Figure 6e) in comparison to synthetic brine water [12,68,69]. It is important to highlight that in the case of an industrial scale module, the circulation pump generates a specific level of overpressure to induce deformation at the water–air interface, resulting in the wetting of the membrane. Consequently, this leads to a nonslip condition, followed by fouling [70]. Regarding the fouling phenomena, the prevention of fouling/scaling in MD membranes can be significantly delayed by implementing superhydrophobic or omniphobic membranes. This approach holds great significance in terms of the development of materials and continues to be a crucial area of focus. The utilization of pre-treatment techniques, including flocculation, water softening, micro- or nano-filtration, and pH regulation, plays a crucial role in effectively inhibiting the formation of membranes at a reduced cost could be achieved with the advancement of fouling-resistant membranes [67]. To ensure the sustained and stable operation of the MD process, it is necessary to undertake pre-treatment of the seawater, employ membrane cleaning techniques, and enhance the structure of the membrane [71–73].

Table 4. Specification of desalinated seawater by DCMD.

Parameter	Value
EC (μS/cm)	133
TDS (mg/L)	86
pH	6.66
Salinity (psu)	0
Turbidity (NTU)	0.80

In Table 5, the DCMD process was compared to the AGMD process based on process similarity. The simplicity of the DCMD process and the type of module in this study were the reasons for its superiority compared to AGMD. In contrast to some studies, inexpensive materials were used to make the calcium carbonate composite substrate, as well as affordable alumina materials for the coating layer in order to achieve ceramic membranes with suitable prices and characteristics for the membrane distillation process. HDTMS as a fluorine-free hydrophobic agent, compared to other studies with lower cost and fewer environmental effects, had an effective performance in the hydrophobicity of the produced membranes.

Table 5. Literature on ceramic membrane performance on membrane distillation process.

Membrane	Hydrophobic Agent	Feed Solution	Feed/Permeate Temperature (°C)	Flux (kg/m ² ·h)	Salt Rejection (R%)	Membrane Configuration	Application	Ref.
alumina and zirconia membranes	FAS	NaCl (0.01–1 molarity)	95/5	0.87–5.4	~100	Tubular	DCMD	[74]
Tunisian clay	FAS	NaCl solution	90/5	3.2-6.45	99	planar	AGMD	[75]
Titania	FAS	NaCl solution	90/5	1.2	N/A	Tubular	AGMD	[40]
Al ₂ O ₃ /TiO ₂ / ZrO ₂	HDTMS	NaCl (0.25–1 M)	72/5	0.31-8.95	99	Tubular	AGMD	[76]
Ball clay	ZnO nanoparticles with T-PFOS	NaCl solution	80/10	6.2	>99.8	Hollow fibre	DCMD	[77]
Cenosphere	PDMS	NaCl solution	85/5	1–13	99	N/A	DCMD	[78]
Alumina layer on the composite mullite CaCO ₃ synthesis membrane	HDTMS	3.5 wt% NaCl solution	68/15	2.2–3.6	99.60	Tubular	DCMD	This work

According to the temperature column provided in Table 5, it is evident that both the feed-side temperature and the permeate-side temperature have a significant impact on the system flux. Therefore, in order to compare the flux of the present membranes with similar studies, it is important to take into account the influence of temperatures on flux along with other factors as well. In this present work, the feed temperature was maintained at 68 °C while the permeate temperature ranged from 15 to 20 °C.

3.6. Cost Analysis Based on Raw Material and Process

The practical feasibility of any process relies heavily on the analysis of its cost. In our study, we meticulously computed the expenses associated with the raw materials utilized in the production of ceramic membranes. The results, presented in Table 6, indicate that the cost of raw materials for manufacturing ceramic membranes amounted to 0.45 \$ per m^2 of membrane. Consequently, based on our cost analysis, we can confidently assert that the raw material expenses for ceramic membranes are affordable and can be readily employed for water desalination purposes. In the case of decreasing the total process cost, which included process energy cost in addition to the cost-effective raw materials that were utilized to fabricate the ceramic membrane, energy cost could be reduced by utilizing waste heat energy, geothermal energy, and solar energy [79,80].

Table 6. Cost analysis of raw material and energy consumption for water desalination process.

Cost of Raw Material (\$/kg)	Composite Membrane Preparation Cost (\$/m ²)	Cost of Consumption Energy in Sintering Process (\$/m ²)	of Consumption rgy in Sintering rocess (\$/m ²) Total Ceramic Membrane Preparation Cost (\$/m ²)	
0.1	0.45	0.09	0.54	0.0005

Notes: Total cost of membrane preparation: Ref [81]: 130 m^2 , Ref [82]: 220 m^2 , Ref [83]: 130 m^2 , Ref [84]: 78 m^2 . In the given ceramic works, the cost of energy consumption of the process is not reported.

4. Conclusions

In this study, we investigated the fabrication and green surface modification of costeffective tubular ceramic membranes by dip-coating them in an HDTMS ethanol solution to enhance the durability of membrane hydrophobicity under a DCMD performance test. We used a 1-µm layer on the membrane surface to prevent pore wetting. An average permeate flux of $3.15 \text{ kg/(m^2 \cdot h)}$ and R% of 99.62% were found for the 3.5 wt.%. NaCl solution for a 5.5-h test without any pore wetting. The selected membrane also showed satisfying results on seawater desalination, bringing significant results in desalination and reducing seawater turbidity up to 93.13%. In conclusion, several results were obtained from the experiments conducted. Firstly, it was found that HDTMS was a suitable grafting agent that could effectively enhance membrane hydrophobicity with a contact angle of 160°. To ensure that the M2 membrane can be used as an alternative membrane in membrane distillation, surface layering was applied to reduce the surface roughness. Additionally, high-salt rejection was observed in the M2 membrane sample, indicating that the combination of HDTMS and an alumina-coated layer had a positive effect on surface hydrophobization. The remarkable durability of the altered membrane was attributed to the results obtained from various tests, including the contact angle test, FESEM, LEP test, FTIR analysis, and assessment of the membrane's permeability. A crucial aspect that often receives less attention in the research is the temperature of the permeate side, which should not be excessively low or impractical. The permeate temperature was influenced by the lowest temperature within the system, which was determined by the ambient temperature. However, the trend of the flux descended, but approached a plateau. An attempt will be made to maintain the flux as a function of time in our future work. Additionally, applying fouling inorganic and organic agents to study the fouling phenomenon will be considered in our future work.

Author Contributions: Conceptualization, J.Z. and M.A. (Mohsen Abbasi), methodology, J.Z. and M.A. (Mohsen Abbasi); software, J.Z. and M.A. (Mohsen Abbasi); validation, J.Z., M.A. (Mohsen Abbasi) and M.D.; formal analysis, J.Z., M.A. (Mohsen Abbasi), S.A.H. and M.A. (Mohammad Akrami); investigation, J.Z., M.A. (Mohsen Abbasi) and S.A.H.; resources, M.A. (Mohsen Abbasi); data curation, J.Z. and M.A. (Mohsen Abbasi); writing—original draft preparation, J.Z.; writing—review and editing, J.Z., M.A. (Mohsen Abbasi), N.D., M.D. and M.A. (Mohammad Akrami); visualization, J.Z. and M.A. (Mohsen Abbasi); supervision, M.A. (Mohsen Abbasi); project administration, M.A. (Mohsen Abbasi) and M.A. (Mohsen Abbasi); authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

Conflicts of Interest: The authors declare no conflicts of interest.

References

- Hubadillah, S.K.; Tai, Z.S.; Othman, M.H.D.; Harun, Z.; Jamalludin, M.R.; Rahman, M.A.; Jaafar, J.; Ismail, A.F. Hydrophobic ceramic membrane for membrane distillation: A mini review on preparation, characterization, and applications. *Sep. Purif. Technol.* 2019, 217, 71–84. [CrossRef]
- 2. Bandar, K.B.; Alsubei, M.D.; Aljlil, S.A.; Darwish, N.B.; Hilal, N. Membrane distillation process application using a novel ceramic membrane for Brackish water desalination. *Desalination* **2021**, *500*, 114906. [CrossRef]
- 3. Tai, Z.S.; Abd Aziz, M.H.; Othman, M.H.D.; Mohamed Dzahir, M.I.H.; Hashim, N.A.; Koo, K.N.; Hubadillah, S.K.; Ismail, A.F.; A Rahman, M.; Jaafar, J. Ceramic membrane distillation for desalination. *Sep. Purif. Rev.* **2020**, *49*, 317–356. [CrossRef]
- 4. Alihemati, Z.; Hashemifard, S.; Matsuura, T.; Ismail, A.; Hilal, N. Current status and challenges of fabricating thin film composite forward osmosis membrane: A comprehensive roadmap. *Desalination* **2020**, *491*, 114557. [CrossRef]
- Twibi, M.F.; Othman, M.H.D.; Hubadillah, S.K.; Alftessi, S.A.; Adam, M.R.B.; Ismail, A.F.; Rahman, M.A.; Jaafar, J.; Raji, Y.O.; Abd Aziz, M.H. Hydrophobic mullite ceramic hollow fibre membrane (Hy-MHFM) for seawater desalination via direct contact membrane distillation (DCMD). *J. Eur. Ceram. Soc.* 2021, *41*, 6578–6585. [CrossRef]
- Subramani, A.; Jacangelo, J.G. Emerging desalination technologies for water treatment: A critical review. Water Res. 2015, 75, 164–187. [CrossRef] [PubMed]
- 7. Wang, P.; Chung, T.-S. Recent advances in membrane distillation processes: Membrane development, configuration design and application exploring. *J. Membr. Sci.* 2015, 474, 39–56. [CrossRef]
- 8. Ferreira, R.K.M.; Ramlow, H.; Marangoni, C.; Machado, R.A.F. A review on the manufacturing techniques of porous hydrophobic ceramic membranes applied to direct contact membrane distillation. *Adv. Appl. Ceram.* **2021**, *120*, 336–357. [CrossRef]
- Dow, N.; García, J.V.; Niadoo, L.; Milne, N.; Zhang, J.; Gray, S.; Duke, M. Demonstration of membrane distillation on textile waste water: Assessment of long term performance, membrane cleaning and waste heat integration. *Environ. Sci. Water Res. Technol.* 2017, 3, 433–449. [CrossRef]
- 10. Khayet, M.; Souhaimi, M.K.; Matsuura, T. Membrane Distillation: Principles and Applications; Elsevier: Amsterdam, The Netherlands, 2011.
- 11. Drioli, E.; Ali, A.; Macedonio, F. Membrane distillation: Recent developments and perspectives. *Desalination* **2015**, *356*, 56–84. [CrossRef]
- 12. He, F.; Gilron, J.; Lee, H.; Song, L.; Sirkar, K.K. Potential for scaling by sparingly soluble salts in crossflow DCMD. *J. Membr. Sci.* **2008**, *311*, 68–80. [CrossRef]
- 13. Deshmukh, A.; Boo, C.; Karanikola, V.; Lin, S.; Straub, A.P.; Tong, T.; Warsinger, D.M.; Elimelech, M. Membrane distillation at the water-energy nexus: Limits, opportunities, and challenges. *Energy Environ. Sci.* **2018**, *11*, 1177–1196. [CrossRef]
- 14. Dow, N.; Gray, S.; Zhang, J.; Ostarcevic, E.; Liubinas, A.; Atherton, P.; Roeszler, G.; Gibbs, A.; Duke, M. Pilot trial of membrane distillation driven by low grade waste heat: Membrane fouling and energy assessment. *Desalination* **2016**, *391*, 30–42. [CrossRef]
- 15. Chen, X.; Gao, X.; Fu, K.; Qiu, M.; Xiong, F.; Ding, D.; Cui, Z.; Wang, Z.; Fan, Y.; Drioli, E. Tubular hydrophobic ceramic membrane with asymmetric structure for water desalination via vacuum membrane distillation process. *Desalination* **2018**, 443, 212–220. [CrossRef]
- 16. Wang, J.-W.; Li, L.; Zhang, J.-W.; Xu, X.; Chen, C.-S. β-Sialon ceramic hollow fiber membranes with high strength and low thermal conductivity for membrane distillation. *J. Eur. Ceram. Soc.* **2016**, *36*, 59–65. [CrossRef]
- 17. Ramlow, H.; Machado, R.A.F.; Marangoni, C. Direct contact membrane distillation for textile wastewater treatment: A state of the art review. *Water Sci. Technol.* 2017, *76*, 2565–2579. [CrossRef] [PubMed]
- 18. Tijing, L.D.; Woo, Y.C.; Choi, J.-S.; Lee, S.; Kim, S.-H.; Shon, H.K. Fouling and its control in membrane distillation—A review. *J. Membr. Sci.* 2015, 475, 215–244. [CrossRef]
- 19. Li, F.; Huang, J.; Xia, Q.; Lou, M.; Yang, B.; Tian, Q.; Liu, Y. Direct contact membrane distillation for the treatment of industrial dyeing wastewater and characteristic pollutants. *Sep. Purif. Technol.* **2018**, *195*, 83–91. [CrossRef]

- Hashemifard, S.A.; Abdoli, A.; Khosravi, A.; Matsuura, T.; Abbasi, M. Predicting and evaluating the performance of DCMD: The effect of non-ideal morphology and thermal conductivity of porous nanocomposite membranes. *Chem. Eng. Res. Des.* 2023, 192, 638–652. [CrossRef]
- Hakami, M.W.; Alkhudhiri, A.; Al-Batty, S.; Zacharof, M.-P.; Maddy, J.; Hilal, N. Ceramic microfiltration membranes in wastewater treatment: Filtration behavior, fouling and prevention. *Membranes* 2020, 10, 248. [CrossRef]
- 22. Kayvani Fard, A.; McKay, G.; Buekenhoudt, A.; Al Sulaiti, H.; Motmans, F.; Khraisheh, M.; Atieh, M. Inorganic membranes: Preparation and application for water treatment and desalination. *Materials* **2018**, *11*, 74. [CrossRef]
- 23. Wang, J.-W.; Li, X.-Z.; Fan, M.; Gu, J.-Q.; Hao, L.-Y.; Xu, X.; Chen, C.-S.; Wang, C.-M.; Hao, Y.-Z.; Agathopoulos, S. Porous β-Sialon planar membrane with a robust polymer-derived hydrophobic ceramic surface. *J. Membr. Sci.* **2017**, 535, 63–69. [CrossRef]
- 24. Kumar, R.V.; Goswami, L.; Pakshirajan, K.; Pugazhenthi, G. Dairy wastewater treatment using a novel low cost tubular ceramic membrane and membrane fouling mechanism using pore blocking models. J. Water Process Eng. 2016, 13, 168–175. [CrossRef]
- Song, I.-H.; Bae, B.-S.; Ha, J.-H.; Lee, J. Effect of hydraulic pressure on alumina coating on pore characteristics of flat-sheet ceramic membrane. *Ceram. Int.* 2017, 43, 10502–10507. [CrossRef]
- Hubadillah, S.K.; Othman, M.H.D.; Ismail, A.; Rahman, M.A.; Jaafar, J. A low cost hydrophobic kaolin hollow fiber membrane (h-KHFM) for arsenic removal from aqueous solution via direct contact membrane distillation. *Sep. Purif. Technol.* 2019, 214, 31–39. [CrossRef]
- 27. Mittal, P.; Jana, S.; Mohanty, K. Synthesis of low-cost hydrophilic ceramic–polymeric composite membrane for treatment of oily wastewater. *Desalination* **2011**, *282*, 54–62. [CrossRef]
- 28. Hedfi, I.; Hamdi, N.; Rodriguez, M.; Srasra, E. Development of a low cost micro-porous ceramic membrane from kaolin and Alumina, using the lignite as porogen agent. *Ceram. Int.* **2016**, *42*, 5089–5093. [CrossRef]
- Kasprzhitskii, A.; Lazorenko, G.; Yavna, V.; Daniel, P. DFT theoretical and FT-IR spectroscopic investigations of the plasticity of clay minerals dispersions. J. Mol. Struct. 2016, 1109, 97–105. [CrossRef]
- 30. Cabassud, C.; Wirth, D. Membrane distillation for water desalination: How to chose an appropriate membrane? *Desalination* **2003**, 157, 307–314. [CrossRef]
- Sarbatly, R.; Chiam, C.-K. Evaluation of geothermal energy in desalination by vacuum membrane distillation. *Appl. Energy* 2013, 112, 737–746. [CrossRef]
- 32. Suárez, F.; Tyler, S.W. Comments on "Evaluation of systems coupling vacuum membrane distillation and solar energy for seawater desalination". *Chem. Eng. J.* 2011, 178, 475–476. [CrossRef]
- 33. Zrelli, A.; Chaouachi, B. Modeling and simulation of a vacuum membrane distillation plant coupled with solar energy and using helical hollow fibers. *Braz. J. Chem. Eng.* 2019, *36*, 1119–1129. [CrossRef]
- 34. Mao, Y.; Huang, Q.; Meng, B.; Zhou, K.; Liu, G.; Gugliuzza, A.; Drioli, E.; Jin, W. Roughness-enhanced hydrophobic graphene oxide membrane for water desalination via membrane distillation. *J. Membr. Sci.* **2020**, *611*, 118364. [CrossRef]
- Omar, N.M.A.; Othman, M.H.D.; Tai, Z.S.; Kurniawan, T.A.; El-badawy, T.; Goh, P.S.; Othman, N.H.; Rahman, M.A.; Jaafar, J.; Ismail, A.F. Bottlenecks and recent improvement strategies of ceramic membranes in membrane distillation applications: A review. J. Eur. Ceram. Soc. 2022, 42, 5179–5194. [CrossRef]
- Song, Y.; Chen, Z.; Chen, J.-H. Preparation and characterisation of the novel hydrophobic FAS/α-Al₂O₃ composite membrane for membrane distillation. *Mater. Res. Innov.* 2022, 26, 168–175. [CrossRef]
- Hubadillah, S.K.; Othman, M.H.D.; Gani, P.; Sunar, N.M.; Tai, Z.S.; Koo, K.N.; Pauzan, M.A.B.; Ismail, N.J.; Zahari, S.S.N.S. Integrated green membrane distillation-microalgae bioremediation for arsenic removal from Pengorak River Kuantan, Malaysia. *Chem. Eng. Process. Process Intensif.* 2020, 153, 107996. [CrossRef]
- García-Fernández, L.; Wang, B.; García-Payo, M.; Li, K.; Khayet, M. Morphological design of alumina hollow fiber membranes for desalination by air gap membrane distillation. *Desalination* 2017, 420, 226–240. [CrossRef]
- Zhang, J.-W.; Fang, H.; Wang, J.-W.; Hao, L.-Y.; Xu, X.; Chen, C.-S. Preparation and characterization of silicon nitride hollow fiber membranes for seawater desalination. J. Membr. Sci. 2014, 450, 197–206. [CrossRef]
- 40. Kujawa, J.; Cerneaux, S.; Kujawski, W. Investigation of the stability of metal oxide powders and ceramic membranes grafted by perfluoroalkylsilanes. *Colloids Surf. A Physicochem. Eng. Asp.* **2014**, 443, 109–117. [CrossRef]
- Dhore, R.; Murthy, G.S. Per/polyfluoroalkyl substances production, applications and environmental impacts. *Bioresour. Technol.* 2021, 341, 125808. [CrossRef]
- Calvert, L.; Green, M.P.; De Iuliis, G.N.; Dun, M.D.; Turner, B.D.; Clarke, B.O.; Eamens, A.L.; Roman, S.D.; Nixon, B. Assessment of the emerging threat posed by perfluoroalkyl and polyfluoroalkyl substances to Male reproduction in humans. *Front. Endocrinol.* 2022, 12, 799043. [CrossRef]
- 43. Nayak, S.; Sahoo, G.; Das, I.I.; Mohanty, A.K.; Kumar, R.; Sahoo, L.; Sundaray, J.K. Poly-and Perfluoroalkyl Substances (PFAS): Do They Matter to Aquatic Ecosystems? *Toxics* 2023, *11*, 543. [CrossRef] [PubMed]
- Cong, S.; Liu, X.; Guo, F. Membrane distillation using surface modified multi-layer porous ceramics. *Int. J. Heat Mass Transf.* 2019, 129, 764–772. [CrossRef]
- 45. Falamaki, C.; Naimi, M.; Aghaie, A. Dual behavior of CaCO3 as a porosifier and sintering aid in the manufacture of alumina membrane/catalyst supports. *J. Eur. Ceram. Soc.* 2004, 24, 3195–3201. [CrossRef]

- Jafari, B.; Rezaei, E.; Abbasi, M.; Hashemifard, S.A.; Sillanpää, M. Application of mullite-zeolite-alumina microfiltration membranes coated by SiO2 nanoparticles for separation of oil-in-water emulsions. *J. Eur. Ceram. Soc.* 2022, 42, 6005–6014. [CrossRef]
- Ren, T.; Tang, G.; Yuan, B.; Yang, Y.; Yan, Z.; Ma, L.; Huang, X. Hexadecyltrimethoxysilane-Modified SiO2 Nanoparticle-Coated Halloysite Nanotubes Embedded in Silicone–Acrylic Polymer Films as Durable Fluorine-Free Superhydrophobic Coatings. ACS Appl. Nano Mater. 2020, 3, 5807–5815. [CrossRef]
- Alftessi, S.A.; Othman, M.H.D.; Adam, M.R.B.; Farag, T.M.; Tai, Z.S.; Raji, Y.O.; Rahman, M.A.; Jaafar, J.; Ismail, A.F.; Bakar, S.A. Hydrophobic silica sand ceramic hollow fiber membrane for desalination via direct contact membrane distillation. *Alex. Eng. J.* 2022, *61*, 9609–9621. [CrossRef]
- 49. Rasouli, Y.; Abbasi, M.; Hashemifard, S.A. Investigation of in-line coagulation-MF hybrid process for oily wastewater treatment by using novel ceramic membranes. *J. Clean. Prod.* 2017, *161*, 545–559. [CrossRef]
- 50. Yousefi, M.; Abbasi, M.; Akrami, M.; Sillanpää, M. Pre-Treatment and Turbidity Reduction of Sea Waters Using New Composite Ceramic Microfiltration Membranes with Iron Oxide Additive. *Water* **2022**, *14*, 3475. [CrossRef]
- Jafari, B.; Abbasi, M.; Hashemifard, S.A.; Sillanpää, M. Elaboration and characterization of novel two-layer tubular ceramic membranes by coating natural zeolite and activated carbon on mullite-alumina-zeolite support: Application for oily wastewater treatment. J. Asian Ceram. Soc. 2020, 8, 848–861. [CrossRef]
- 52. Abid, M.B.; Wahab, R.A.; Salam, M.A.; Moujdin, I.A.; Gzara, L. Desalination technologies, membrane distillation, and electrospinning, an overview. *Heliyon* 2023, 9, e12810. [CrossRef] [PubMed]
- 53. Moghadam, A.M.; Salehi, M.B. Enhancing hydrocarbon productivity via wettability alteration: A review on the application of nanoparticles. *Rev. Chem. Eng.* 2019, *35*, 531–563. [CrossRef]
- 54. Morrow, N.R. Wettability and its effect on oil recovery. J. Pet. Technol. 1990, 42, 1476–1484. [CrossRef]
- 55. Chen, H.; Muros-Cobos, J.L.; Amirfazli, A. Contact angle measurement with a smartphone. *Rev. Sci. Instrum.* **2018**, *89*, 035117. [CrossRef] [PubMed]
- Huhtamaki, T.; Tian, X.; Korhonen, J.T.; Ras, R.H. Surface-wetting characterization using contact-angle measurements. *Nat. Protoc.* 2018, 13, 1521–1538. [CrossRef]
- 57. Bwatanglang, I.B.; Magili, S.T.; Kaigamma, I. Adsorption of phenol over bio-based silica/calcium carbonate (CS-SiO₂/CaCO₃) nanocomposite synthesized from waste eggshells and rice husks. *PeerJ Phys. Chem.* **2021**, *3*, e17. [CrossRef]
- 58. Netala, V.R.; Kotakadi, V.S.; Nagam, V.; Bobbu, P.; Ghosh, S.B.; Tartte, V. First report of biomimetic synthesis of silver nanoparticles using aqueous callus extract of Centella asiatica and their antimicrobial activity. *Appl. Nanosci.* **2015**, *5*, 801–807. [CrossRef]
- 59. Suegama, P.H.; Aoki, I.V. Electrochemical behavior of carbon steel pre-treated with an organo functional bis-silane filled with copper phthalocyanine. *J. Braz. Chem. Soc.* **2008**, *19*, 744–754. [CrossRef]
- 60. Zeng, Y.-X.; Zhong, X.-W.; Liu, Z.-Q.; Chen, S.; Li, N. Preparation and Enhancement of Thermal Conductivity of Heat Transfer Oil-Based MoS2Nanofluids. J. Nanomater. 2013, 2013, 1–6. [CrossRef]
- Capeletti, L.B.; Zimnoch, J.ú.H. Fourier transform infrared and Raman characterization of silica-based materials. *Appl. Mol. Spectrosc. Curr. Res. Chem. Biol. Sci.* 2016, 32, 137–144.
- 62. Jozanikohan, G.; Abarghooei, M.N. The Fourier transform infrared spectroscopy (FTIR) analysis for the clay mineralogy studies in a clastic reservoir. *J. Pet. Explor. Prod. Technol.* **2022**, *12*, 2093–2106. [CrossRef]
- 63. Fang, H.; Gao, J.; Wang, H.; Chen, C. Hydrophobic porous alumina hollow fiber for water desalination via membrane distillation process. *J. Membr. Sci.* 2012, 403, 41–46. [CrossRef]
- 64. Yusof, N.; Rana, D.; Ismail, A.F.; Matsuura, T. Microstructure of polyacrylonitrile-based activated carbon fibers prepared from solvent-free coagulation process. *J. Appl. Res. Technol.* **2016**, *14*, 54–61. [CrossRef]
- Hubadillah, S.K.; Othman, M.H.D.; Matsuura, T.; Rahman, M.A.; Jaafar, J.; Ismail, A.; Amin, S.Z.M. Green silica-based ceramic hollow fiber membrane for seawater desalination via direct contact membrane distillation. *Sep. Purif. Technol.* 2018, 205, 22–31. [CrossRef]
- 66. Gryta, M. Fouling in direct contact membrane distillation process. J. Membr. Sci. 2008, 325, 383–394. [CrossRef]
- 67. Liu, L.; Xiao, Z.; Liu, Y.; Li, X.; Yin, H.; Volkov, A.; He, T. Understanding the fouling/scaling resistance of superhydrophobic/omniphobic membranes in membrane distillation. *Desalination* **2021**, *499*, 114864. [CrossRef]
- 68. Rezaei, M.; Alsaati, A.; Warsinger, D.M.; Hell, F.; Samhaber, W.M. Long-running comparison of feed-water scaling in membrane distillation. *Membranes* **2020**, *10*, 173. [CrossRef] [PubMed]
- 69. Santos, P.G.; Scherer, C.M.; Fisch, A.G.; Rodrigues, M.A.S. Membrane Distillation: Pre-Treatment Effects on Fouling Dynamics. *Membranes* **2021**, *11*, 958. [CrossRef]
- Song, L.; Ma, Z.; Liao, X.; Kosaraju, P.B.; Irish, J.R.; Sirkar, K.K. Pilot plant studies of novel membranes and devices for direct contact membrane distillation-based desalination. *J. Membr. Sci.* 2008, 323, 257–270. [CrossRef]
- Meng, Y.; Zhong, Q.; Liu, Y.; Yan, Z.; Liang, Y.; Chang, H.; Liang, H.; Vidic, R.D. Evaluating membrane cleaning for organic fouling in direct contact membrane distillation. *J. Clean. Prod.* 2023, 410, 137319. [CrossRef]
- 72. Abdel-Karim, A.; Leaper, S.; Skuse, C.; Zaragoza, G.; Gryta, M.; Gorgojo, P. Membrane cleaning and pretreatments in membrane distillation–a review. *Chem. Eng. J.* 2021, 422, 129696. [CrossRef]
- 73. Chang, H.; Zhu, Y.; Huang, L.; Yan, Z.; Qu, F.; Liang, H. Mineral scaling induced membrane wetting in membrane distillation for water treatment: Fundamental mechanism and mitigation strategies. *Water Res.* **2023**, 247, 120807. [CrossRef] [PubMed]

- 74. Larbot, A.; Gazagnes, L.; Krajewski, S.; Bukowska, M.; Kujawski, W. Water desalination using ceramic membrane distillation. *Desalination* **2004**, *168*, 367–372. [CrossRef]
- 75. Khemakhem, S.; Amar, R.B. Modification of Tunisian clay membrane surface by silane grafting: Application for desalination with Air Gap Membrane Distillation process. *Colloids Surf. A Physicochem. Eng. Asp.* **2011**, *387*, 79–85. [CrossRef]
- Kujawa, J. From nanoscale modification to separation-The role of substrate and modifiers in the transport properties of ceramic membranes in membrane distillation. J. Membr. Sci. 2019, 580, 296–306. [CrossRef]
- 77. Abd Aziz, M.H.; Pauzan, M.A.B.; Hisam, N.A.S.M.; Othman, M.H.D.; Adam, M.R.; Iwamoto, Y.; Puteh, M.H.; Rahman, M.A.; Jaafar, J.; Ismail, A.F. Superhydrophobic ball clay based ceramic hollow fibre membrane via universal spray coating method for membrane distillation. *Sep. Purif. Technol.* 2022, 288, 120574. [CrossRef]
- 78. Lanjewar, T.; Satyakam, A.; Varma, M.N. Low-Cost Hydrophobic Cenosphere Ceramic Membrane for the Desalination Application Using Direct Contact Membrane Distillation. *Arab. J. Sci. Eng.* **2022**, *47*, 6445–6460. [CrossRef]
- 79. Gontarek-Castro, E.; Castro-Muñoz, R. How to make membrane distillation greener: A review of environmentally friendly and sustainable aspects. *Green Chem.* 2024, 26, 164–185. [CrossRef]
- Yadav, A.; Labhasetwar, P.K.; Shahi, V.K. Membrane distillation using low-grade energy for desalination: A review. J. Environ. Chem. Eng. 2021, 9, 105818. [CrossRef]
- 81. Nandi, B.; Uppaluri, R.; Purkait, M. Preparation and characterization of low cost ceramic membranes for micro-filtration applications. *Appl. Clay Sci.* 2008, 42, 102–110. [CrossRef]
- 82. Cassano, A.; Marchio, M.; Drioli, E. Clarification of blood orange juice by ultrafiltration: Analyses of operating parameters, membrane fouling and juice quality. *Desalination* **2007**, *212*, 15–27. [CrossRef]
- 83. Vasanth, D.; Pugazhenthi, G.; Uppaluri, R. Biomass assisted microfiltration of chromium (VI) using Baker's yeast by ceramic membrane prepared from low cost raw materials. *Desalination* **2012**, *285*, 239–244. [CrossRef]
- 84. Emani, S.; Uppaluri, R.; Purkait, M.K. Preparation and characterization of low cost ceramic membranes for mosambi juice clarification. *Desalination* **2013**, *317*, 32–40. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.