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Grafting of low cost ultrafiltration ceramic membrane by Tunisian olive oil molecules and application to air gap membrane distillation

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ABSTRACT

Grafting is probably one of the most important means to be considered in order to change the hydrophilic character of ceramic membranes into hydrophobic ones. In this context, the surface properties of a composite ultrafiltration membrane elaborated from the mud of hydrocyclone laundries of phosphates, having an average pore diameter of 11 nm and a layer thickness of around 9 µm, were chemically modified by grafting Tunisian olive oil molecules. Grafting process efficiency was characterized by contact angle measurements, Fourier transform infrared spectroscopy, nitrogen adsorption/desorption method and membrane permeability. It was found that the contact angle value increases from 16° before grafting to 121° after grafting showing that grafting leads to high membrane hydrophobicity. The determination of water permeability shows a high decrease from 90 L/hm^2 bar to 7 L/hm^2 bar, before and after grafting, respectively. The new hydrophobic ceramic membrane seems to be promising in the field of membrane distillation using seawater desalination. The salt rejection obtained using grafted UF membrane was 99%.

Keywords: Ultrafiltration membrane; Grafting; Olive oil; Membrane distillation

1. Introduction

At present, a growing interest is focused towards the development of porous inorganic membranes that can provide better selectivity, thermal and chemical stability than organic membranes. Thus, attention is particularly turned on preparation of low cost membranes made from abundant natural materials such as clay [1–3], ash [4,5], apatite [6], and mud [7]. They can be easily applied in many areas of water treatment. These membranes originally have a hydrophilic character due to the presence of surface hydroxyl groups [8–10]. Grafting process of specific molecules can be used to increase the hydrophobicity of these membranes with the objective to extend their application field.

Various kinds of molecules going from natural compounds to hydrophobic chemicals may be grafted directly on metallic oxide powders or on membrane surfaces. In this context, many research groups have been working on surface modification to enhance the hydrophobic feature of mineral membrane materials. Kujawa et al. [11] realized the grafting process using two types of perfluoroalkylsilanes (PFAS) molecules characterized by a different fluorinated carbon chain length (1H,1H,2H,2H-perfluorooctyltriethoxysilane (C6) and 1H,1H,2H,2H-perfluorotetradecyltriethoxysilane (C12) to modify three types of powders made from alumina, zirconia and titania. The highest grafting efficiency was noticed for alumina membrane thanks to its highest specific surface area. Hendren et al. [12] reported the modification of alumina ceramic membranes with different surface modifying agents: 1H,1H,2H,2H-perfluorodecyltriethoxysilane (PFS), tri-

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chloromethylsilane (TCS), and trimethylchlorosilane (TMS) and their application in direct contact membrane distillation (DCMD). Zirconia membrane surface was successfully grafted through a graft polymerization using poly(vinylpyrrolidone) (PVP) by Rovira-Bru et al. [13]. Djafer et al. [14] studied the surface modification of titania powders by phosphate and phosphonic acids. Modified titania powders were suitable for photocatalytic activity. A study performed by Khemakhem et al. [15], involved the modification of the surface of a microfiltration Tunisian clay membrane using triethoxy-1H, 1H, 2H, 2H-perfluorodecylsilane (C8). The high hydrophobicity obtained after grafting allows the application for seawater desalination using membrane distillation process. In the literature, there are a few previous works, which studied the modification of membrane surface using oil as grafting agent. It can be noticed particularly work done by Romero et al. [16], who deposited a thin film of a lipidic compound on ceramic macroporous supports to obtain hydrophobic tubular membranes. Based on these considerations, this work studied the hydrophobic character of ceramic ultrafiltration mud/mud membrane obtained by grafting oil onto the membrane.

Hydrophobic ceramic membranes can be successfully applied as non-fouling ceramic membranes [13,17], in water ozonation [18], in pervaporation [19], in the process of extraction by gas [16] and in membrane distillation [20]. Khalifa et al. [21] presented experimental and theoretical studies of the performance of air gap membrane distillation (AGMD) system. They concluded that the measured salt rejection factor is above 99.9%. This value emphasizes the suitability of the AGMD system for desalination of high concentration feeds. Chul Woo et al. [22] used a facile electrospinning technique for preparation of dual-layer nanofiber nonwoven membrane, which was applied for desalination by air gap membrane distillation (AGMD). They found when using a temperature range between 50 and 60°C that the permeate flux and salt rejection were of 15.5 (LMH) and 99.2%, respectively. M. Essalhi et al. [23] made a comparison between two membrane distillation (MD) configurations, liquid gap (LGMD) and air gap (AGMD), using a porous composite hydrophobic/hydrophilic membrane under the same operating parameters. The salt rejection factors were found to be almost similar for both MD variants and higher than 99.6%. B.L. Pangarkar et al. [24] presented a novel multi-effect air gap membrane distillation (ME-AGMD) module, which was successfully developed for the purpose of water treatment. The maximum permeate flux of about 166.4 LMH was achieved at a feed temperature of 80°C, a feed flow rate of 1.5 L/min and a coolant temperature of 20°C. S. Cerneaux et al. [25] studied vacuum membrane distillation (VMD), air gap membrane distillation (AGMD) and direct contact membrane distillation (DCMD) configurations using titania and zirconia membranes chemically modified with triethoxy-1H,1H,2H,2H-perfluorode cylsilane $C_8F_{17}(CH_2)2Si(OC_2H_5)_3$. They evidenced that the salt rejection is strongly dependent of the pore size of the filtration layer and that the air gap mode lead to higher flux compared to VMD and DCMD with rejection rates superior than of 99.5% in all conditions tested.

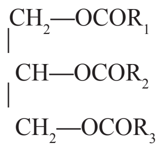
The main objectives of this work were to obtain grafted ultrafiltration mud/mud ceramic membrane using a natural grafting molecule such as olive oil and to determine its properties and performances towards seawater desalination by applying air gap membrane distillation (AGMD) process.

2. Experimental

2.1. Materials

Ceramic ultrafiltration (UF) membrane from phosphates industry sub-product material known as mud was previously prepared in our laboratory from the macroporous support to the ultrafiltration separation layer [7]. The mud support is characterized by an open porosity of 39% and an average pore diameter around 1 µm that is reduced to 11 nm in presence of the mud ultrafiltration layer, giving a water permeability of 90 L/h·m²·bar for an active surface area of 23.37 cm².

Three concentrations of Tunisian olive oil mixed with hexane (0.5 mL/L, 1.4 mL/L and 2.5 mL/L) were chosen for modifying the surface of the membrane. The Tunisian olive oil (triglyceride) has a chemical formula that can be written as follows:



$$\begin{array}{l} CH_2\text{—}OCOR_1 \\ | \\ CH\text{—}OCOR_2 \\ | \\ CH_2\text{—}OCOR_3 \end{array}$$

where R1, R2, R3 represent long alkyl chains of triglycerides.

2.2. Grafting procedure

The surface modification of the UF membrane was comparable to what described in previous works performed by Romero et al. [16]. Prior to chemical modification, the membrane was cleaned in an ultrasonic bath in presence of ethanol and acetone, successively and dried in an oven for 15 min at 100 °C. Grafting occurred by immersion of the ceramic membrane in a solution mixture containing a vegetal oil and a solvent at room temperature for 45 min, immersion time required to reach an adequate coverage (pore filling) of the membrane. To decide which oil should be retained to obtain the most hydrophobic membrane, three different vegetable oils were tested (corn oil, olive oil and almond oil). Two series of experiments were performed in all cases using two solvents: dichloromethane and hexane, characterized by opposite dielectric constants of 9.1 and 1.9 at 25°C, respectively. Finally, membranes were successively placed in an oven for 1 h at a temperature of 75°C to evaporate the solvent, washed in ethanol and in acetone for 15 min and placed again in an oven at 100°C to ensure the total elimination of remaining adsorbed oil. To fully characterize the grafting over the mud material, both planar and tubular membranes were prepared. Initially, experiments were performed in flat membranes to determine the optimum conditions of the grafting procedure. After that, tubular membrane was used for application of the AGMD process. The mechanism of grafting is schematically shown in Fig. 1.

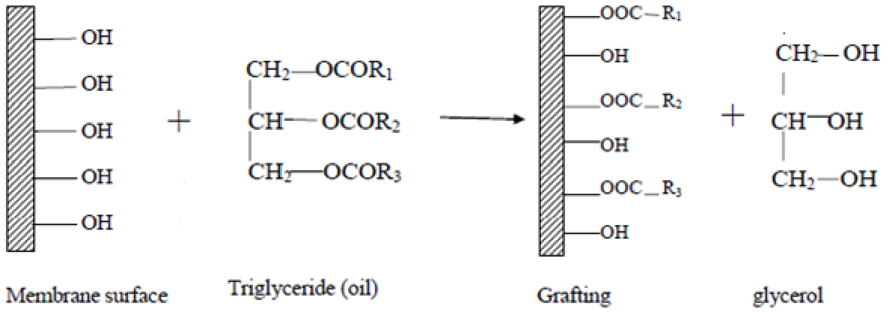


Fig. 1. Proposed reaction scheme of oil molecule with porous mud membrane.

2.3. Characterization techniques

FTIR spectra were obtained using IR spectrophotometer Shimatzu IR 470 to evidence functional groups related to the oil grafting onto the membrane.

Water permeability was measured on grafted and ungrafted ceramic membranes by cross-flow filtration experiments using a home-made pilot plant. Contact angle measurements were performed on planar samples by the water-drop method on a KRUSS apparatus. This technique is efficient to evaluate the hydrophobic character of the membrane. Experiments were done twice on the same samples to give a mean contact angle value with an error of 1°. The nitrogen adsorption/desorption method was used for the determination of the new pore size of the modified mud membrane.

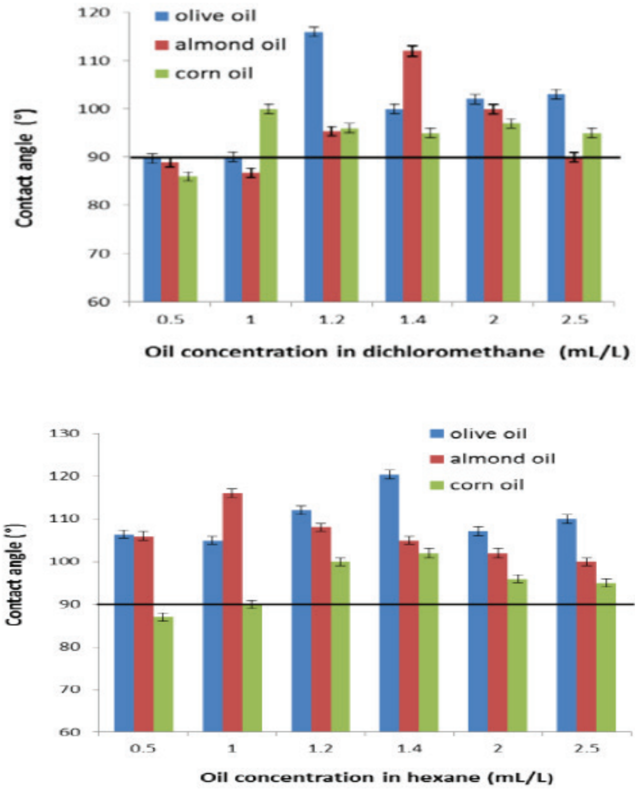


Fig. 2. Evolution of the contact angle values of grafted planar membranes as a function of the concentration of olive, almond and corn oils in: (a) dichloromethane and (b) hexanesolvents.

3. Results and discussion

3.1. Characterization of grafted membrane

A study of the hydrophobicity of the membrane was performed by measuring the contact angle of water drop deposited on planar membranes. In the absence of grafting molecules, the mud membrane is characterized by a contact angle of 16° that is specific of highly hydrophilic membrane material (Fig. 3). In this case, the hydrophilic property is related to the presence of a high hydroxyl group density on the surface of the substrate, mainly composed of silica and calcium oxide [26].

The grafting efficiency of olive, almond and corn oils at various concentrations was tested in presence of dichloromethane and hexane with the objective to define the conditions of grafting leading to the highest contact angle (Fig. 2). It seems that appropriate non-polar solvent such as hexane provides the stronger hydrophobic character in comparison to the polar solvent (dichloromethane). Indeed, the vegetal oils are formed by non-polar molecules, therefore they have a stronger affinity with non-polar organic solvent (hexane).

The contact angle values in the case of olive oil and almond oil dissolved in hexane are close. However, taking into account the importance of olive oil production and industrial transformation in Tunisia, olive oil will be retained as a graft agent in the following work.

From Fig. 3, it can be shown that the contact angle decreased quickly with time during a first period of almost 60 s and then stabilized at 106°, 116° and121° for a concentration of 0.5 mL/L, 1.4 mL/L and 2.5 mL/L, respectively. It appears also that 1.4 mL/L olive oil was the most favorable concentration for the stronger hydrophobic character providing the highest value of contact angle (121°).

To be sure of grafting stability when membrane was in contact of atmosphere, membrane grafted with 1.4 mL/L of olive oil mixed with hexane was kept under controlling conditions of humidity and temperature (20% and 25°C respectively) during six months and then the contact angle was determined again at two periods of one month and six months. The results showed that almost similar contact angles of 121° with an error of 2° were determined.

To prove the presence of the organic species grafted onto the mud membranes, infrared spectra were recorded

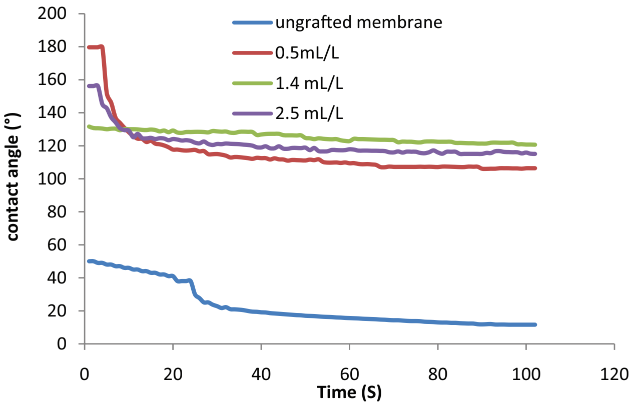


Fig. 3. Evolution of the contact angle with time before and after grafting of planar membranes with olive oil at different concentrations mixed with hexane solvent.

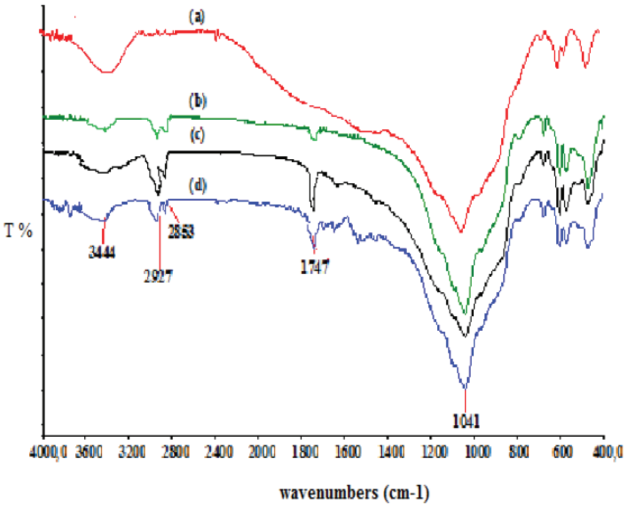


Fig. 4. Infrared spectra of: (a) ungrafted membrane, (b) grafted membrane with olive oil (0.5 mL/L), (c) grafted membrane (1.4 mL/L) and (d) grafted membrane (2.5 mL/L).

(Fig. 4). Within the spectrum of the ungrafted membrane (Fig. 4a), the band at 3444 cm^{-1} is attributed to the stretching vibration peak of OH groups on the membrane surface. After grafting with olive oil, the intensity of this peak decreased showing that grafting did not affect totally the OH groups and then some OH groups did not react with olive oil. This result is consistent with the work done by Gao et al. [27]. The absorption band of strong intensity at 1041 cm^{-1} corresponds to the stretching vibration of Si-O-Si [28] attributed to the membrane composition. Obviously, this band was not affected by the grafting procedure. From the spectrum obtained after grafting (Fig. 4b–d), it can be noticed the appearance of new absorption bands related to the aliphatic moieties CH and CH_2 from the oil which are situated at 2927 cm^{-1} and 2853 cm^{-1}, respectively. In addition, there is an absorption band attributed to the ester group around 1747 cm^{-1}. So, the appearance of these new absorption bands proves that the olive oil grafting didoccur.

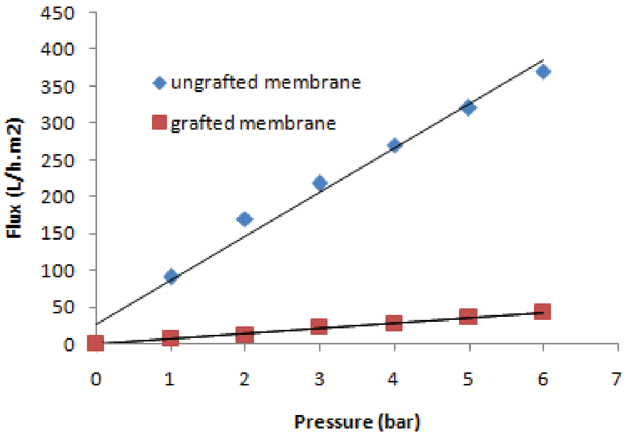


Fig. 5. Evolution of the permeate flux (L/h·m^2) with the applied pressure for the grafted and ungrafted membranes.

In the following study, a mud membrane grafted by 1.4 mL/L of olive oil dissolved in hexane will be chosen as the best hydrophobic membrane.

The water permeability for grafted and ungrafted membranes was determined by plotting the evolutions of the water permeate flux with the transmembrane pressure (TMP) varying in the range 0–6 bar. Fig. 5 shows a linear increase of the permeate flux with transmembrane pressure. This behavior fits well with the Darcy's law:

$$J_w = L_p \Delta P \tag{1}$$

where J_w (L/h·m^2) is the liquid flux through the membrane, L_p (L/h·m^2·bar) is the membrane permeability and ΔP (bar) is the applied transmembrane pressure.

The water permeability decreased from 90 L/h·m^2·bar before grafting to 7 L/h·m^2·bar after grafting. So, it appears that the grafting results in a significant change in membrane proprieties which confirms the hydrophobic character of the membrane.

Pore size distribution of the top layer was obtained from nitrogen adsorption/desorption isotherm using a Quantachrome instruments, the pore diameter was estimated by the BJH (Barret–Joyner–Halenda) method [29]. The pore diameters measured were centered near 2.8 nm after grafting against 11 nm before (Fig. 6). This decrease of average pore size confirms that olive oil molecules were successfully grafted on the membrane surface.

3.2. Application: Air gap membrane distillation(AGMD)

Air gap membrane distillation (AGMD) experiments were performed for seawater desalination using the hydrophobic membrane grafted by 1.4 mL/L olive oil dissolved in hexane to produce drinkable fresh water. The seawater at a concentration of 30 g/L in NaCl was collected from SIDI MANSOUR Sea, located in northern Sfax (Tunisia) and filtered through a 10 µm filter to remove large suspended solids and then used as MD feed without any additional pretreatment. Table 1 shows that the feed water is composed essentially from Cl^-, Na^+, K^+,

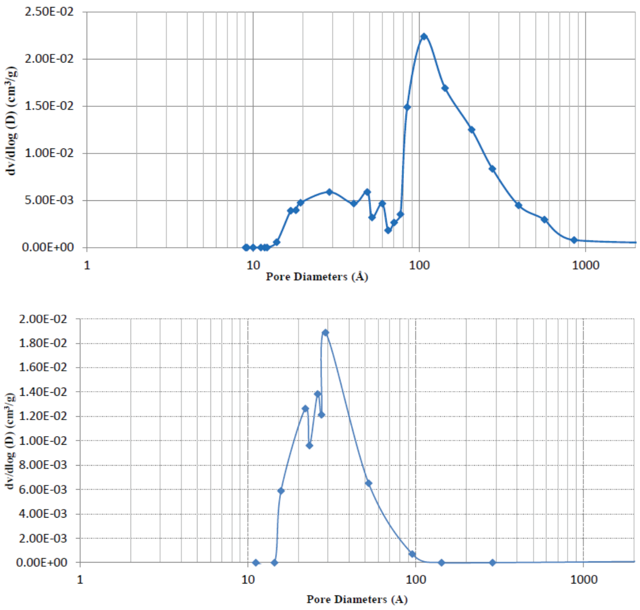


Fig. 6. Nitrogen adsorption–desorption pore size distribution of top layer for the grafted and ungrafted ultrafiltration membrane.

Table 1
Concentration of the important elements in sea water

Components	Concentration (g/l)
Na^+	10.78
Cl^-	19.35
K^+	0.39
Ca^{2+}	0.41
Mg^{2+}	1.2
SO_4^{2-}	2.7

Ca^{2+}, Mg^{2+} and SO_4^{2-}. In normal conditions, the characteristics of the seawater before and after desalination are given in Table 2.

Fig. 7 illustrates the variation of the permeate flux and salt rejection rates as a function of the temperature. Feed temperatures were varied from 75°C to 95°C while keeping the cooling system temperature constant at 5°C. The flow velocity was kept at 2.6 m/s.

As seen, there is an exponential increase of the permeate flux from 70 L/d·m² to 125 L/d·m² with the feed temperature. This behavior is due to the exponential increase of the water vapor pressure with temperature as stated by the Antoine equation:

$$\log\left(\frac{Ps}{P°}\right) = A - \frac{B}{T+C} \tag{2}$$

where Ps is the vapor pressure, $P°$ is the standard pressure, A, B, C are the coefficients of Antoine and T is the temperature. The rejection of salt (R) was calculated according to the following equation:

Table 2
Characteristics of the seawater before and after air gap membrane distillation

Parameters	Salinity (g/l)	Turbidity (NTU)	pH
Feed water	30	15	8.4
Permeate	1.2	0.2	7.2

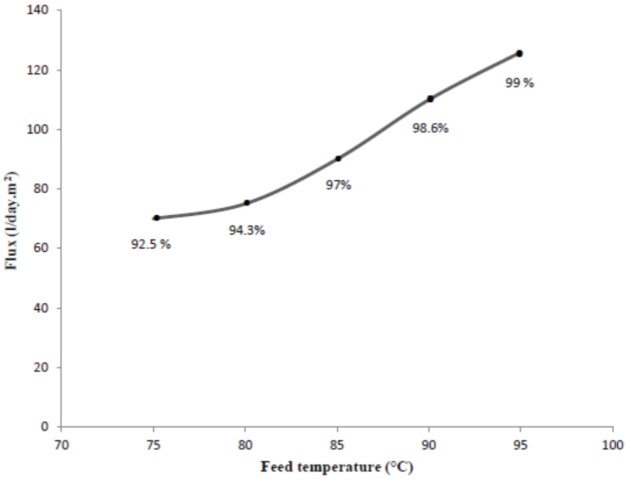


Fig. 7. Variation of the permeate flux of membrane grafted by 1.4 mL/L olive oil dissolved in hexane as a function of the temperature. The values reported on the graph correspond to the salt rejection rates calculated for the grafted membrane after filtration of sea water.

$$R(\%) = \left(1 - \left(\frac{C_p}{C_f}\right)\right) \times 100 \tag{3}$$

where C_f and C_p represent the NaCl concentrations in the feed and permeate solutions, respectively. The salt rejection by AGMD process is about 99% for grafted ceramic membrane. This value below 100% can be explained by the possibility of the salt leakage through some pores. On the other hand, if we compare this result with those obtained by Woo et al. [30] who found salt rejection of almost 100% with using air gap distillation, the difference in salt rejection can be attributed to the high hydrophobic character of Graphene- incorporated nanofiber membrane fabricated by a simple electrospinning technique. Indeed, the determination of the contact angle indicates a value of almost 163° (superhydrophobicity) for this membrane while it was only of 121° for the grafted mud membrane prepared in this work under the optimized conditions.

4. Conclusion

Surface modification of the ceramic ultrafiltration mud/mud membrane by three vegetable oils (corn, olive and almond oils) dissolved in hexane and in dichloromethane at different concentrations was carried out. The grafting changed the ceramic membrane hydrophilic character into hydrophobic one. This study shows that the best grafting efficiency to obtain the stronger hydrophobic property was achieved using 1.4 mL/L olive oil dissolved in hexane. The water contact angle increased from 16° for the original membrane to 121° for the surface modified membrane. The chemical modification was confirmed by FTIR and TGA. In addition, a decrease of average pore size from 11 nm to 2.8 nm before and after surface modification, respectively, proves that olive oil was successfully grafted. The determination of the water permeability of the grafted membrane leads to a value of 7 l/hm^2 bar against 90 l/hm^2 bar for the ungrafted membrane. Due to its strong hydrophobic character, the olive oil molecules grafted membrane was applied to sea water desalination by air gap membrane distillation process (AGMD). A salt rejection rate close to 99% was achieved.

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