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Chapter

Preparation and Evaluation of Hydrophobic Grafted Ceramic Membrane: For Application in Water Desalination

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Abstract

A new inorganic hydrophobic porous membrane was prepared and applied in desalination with the air-gap membrane distillation process. Ceramic supports from low-cost natural Tunisian sand have been elaborated by the extrusion method. The microfiltration layer has been elaborated from ZrO$_2$ powder by slip casting technical using a solution of water, sand powder, and polyvinyl alcohol solution. The hydrophobic surface of the active layer was elaborated by grafting 1H,1H,2H,2H-perfluorodecyltriethoxysilane on the ceramic microfiltration membrane surface (Tunisian Sand/Zirconia), to prepare a hydrophobic surface. The contact angle method allows showing the hydrophobic nature on the grafted membrane surface since it increases from 25° before grafting to values exceeding 140° after grafting. The efficiency of the grafting process was characterized by scanning electron microscopy (SEM). The membrane permeability varies from 700 l.h$^{-1}$.m$^{-2}$ before grafting to 10 l.h$^{-1}$.m$^{-2}$ after grafting. The new hydrophobic membrane seems to be promising in the field of membrane distillation. Salt retention higher than 98% was obtained using a modified microfiltration ceramic membrane.

Keywords: membrane, ceramic, hydrophobic, Tunisian sand, desalination

1. Introduction

Currently, several searches are focusing on the different applications of ceramic membranes [1–3]. The major application fields for ceramic membranes are water purification, pharmaceutical industries, and biotechnology. In this research work, we have prepared a ceramic microfiltration membrane that used the mud of hydrocyclone laundries of phosphates as support, which has very interesting properties in terms of mechanics, chemical resistance, and thermal compared with commercial inorganic ceramic membranes based on pure oxide mineral material such as zirconia, titania, and alumina [4]. Because of the presence of surface hydroxyl groups, these ceramic materials originally have a hydrophilic appearance that can form bonds easily with water molecules [1, 5, 6]. Modifying the hydrophilic character into hydrophobic ceramic membrane is very interesting for several applications. The grafting process
can be performed by reaction between the -OH surface groups of the microfiltration layer and the ethoxy (O-Et) groups of the organosilane, leading to the increase of the hydrophobic properties [5, 7, 8]. Changing the hydrophobicity of the microfiltration layer surface would expand the potential applications of this material. The modification of the microfiltration layer surface allows forming a monomolecular layer of organosilane nature on the ceramic microfiltration layer [9, 10]. Fluoroalkylsilanes are organic groups used to modify the nature of different surfaces and create hydrophobic properties [11–13]. Several researchers have used the transplant process of different fluoroalkylsilanes on the surface of zirconia, silica, titania, and alumina membranes and their applications in different fields [5, 8, 14–16]. The modified inorganic ceramic membranes will be used, for example, in pervaporation and membrane distillation processes. Due to its hydrophobic character, the membrane will not be wet by the aqueous supply solution; then filling of the pores will occur due to capillary forces. The membrane distillation is a thermally driven separation process; in this case, only vapor is transported through a membrane. The membrane distillation technique allows potential applications in several fields of great scientific and industrial interest. It has been used in the treatment and purification of thermally sensitive industrial products such as the concentration of aqueous solution for wastewater treatment [17], water desalination [18–21], fruit juices [22] and in the pharmaceutical industry [23]. The technique of air-gap membrane distillation configuration was used in this work because it is simple to be performed in the laboratory, and it generally produces high water permeate flux. Inorganic ceramic membranes have several advantages in the application of oil-water separation, such as high mechanical strength, chemical inactivity, and thermal stability. Currently, a large amount of oily wastewater is discarded by food industries, petrochemical, and pharmaceutical, leading to further pollution of the environment. Widely used methods of purification of oily wastewater, such as air flotation, gravity separation, coagulation, skimming, and flocculation, have many disadvantages such as high operating costs, low efficiency, corrosion, and recontamination problems [24, 25]. The most widely used techniques are based on the membrane separation process such as dehydration of oil emulsion by pervaporation [26], by reverse osmosis [27], flocculation followed by microfiltration [28], microfiltration alone [29], membrane distillation [30], and ultrafiltration [31].

In this work, a microfiltration membrane prepared of sand/zirconia was surface modified with grafted perfluoroalkyl-silane. Ceramic membranes surface grafted with perfluoroalkyl-silane changed the hydrophilic character into a hydrophobic one. The prepared hydrophobic ceramic membrane was used for water desalination for the air-gap membrane distillation process. It is noted that fresh water can be produced from NaCl solutions as well as seawater.

2. Membrane distillation process

2.1 Principle

Membrane distillation is a thermal membrane process in which a hydrophobic membrane separates a cold and hot stream of water [32, 33]. The hydrophobic property of the membrane stops the passage of liquid water through the pores while allowing the passage of water vapor. The temperature shift between the two membrane surfaces produces a vapor pressure gradient that allows water vapor to cross through the membrane, and finally, the water vapor is condensed on the colder surface.
Finally, we obtained a distillate of very high purity. Membrane distillation may be used in various modes differing, for example, in a protocol of permeates collection [34].

2.2 Air-gap membrane distillation process

In the technical of air-gap membrane distillation (Figure 1), only the effluent to be treated is in contact with the active membrane layer. After crossing the membrane, the vapor permeates passing through the membrane and is condensed on the cold outer surface. There is an air distance between the outer surface of the membrane and the cold surface to reduce the loss of energy by thermal conduction through the membrane. The main male of the air space is that there is an additional resistance to mass transfer. In this technique of distillation, permeate is not in contact with the outer surface of the membrane, there is no fear of wetting the membrane on the permeate side in this process.

3. Experimental

3.1 Reagents

A composite microfiltration membrane mud of Tunisian sand/zirconia with pore diameters in the range of 0.2 μm entirely prepared in our laboratory [35] was used. Every grafting process was performed using 10^{-2} mol.l^{-1} solution of 1H,1H,2H,2H-perfluorodecyltriethoxysilane (97%) supplied from Sigma-Aldrich, it was dissolved in ethanol with an analytical grade of 95% purchased from Chemi-Pharma.

3.2 Preparation and characterizations of hydrophobic membranes

Hydrophobic membranes were prepared by grafting C8 onto the sand/zirconia ceramic membrane. Grafting is performed with several condensation reactions.
between the OH groups found on the membrane surface and the silane functional group. Samples of flat membranes and tubular membranes are fully immersed in fluoroalkylsilanes solutions for 1 h at room temperature. After drying the samplers at 90°C for 1 h, the grafted ceramic membranes were rinsed successively in ethanol and acetone and finally placed in a 100°C oven for 1 h. The contact angles were measured at room temperature (23°C) using a Dataphysics OCA 15 camera with a resolution of 752 to 582 square pixels. The camera is equipped with a CCD camera and operates at an acquisition rate of four frames per second. The surfaces of the samples before and after grafting were characterized by scanning electron microscopy (SEM) (Hitachi S-4500). The pore diameter of the modified microfiltration layer was determined through the nitrogen adsorption/desorption isotherm using the 2010 Asap Micro Metrics Gas Analyzer, the exact diameter of the pores was determined using the BJH (Barret–Joyner–Halenda) method [36]. The permeability was obtained for membranes grafted by a home-made pilot plant.

3.3 Membrane distillation

The setup scheme in Figure 1 was used for the application of grafted membranes in the air-gap membrane distillation process. In this work, the solution to be treated was heated in a stainless steel feed tank and then distributed in the filtration module. The working temperature on the power side ranged from 75 to 95°C, while on the cooling side was kept constant at 5°C. Permeate vapor will be condensed on a surface of cooled stainless steel near the membrane (Figure 1). The temperatures were measured with two thermometers located at the feed cell frame and at the cooling plates. It is noted that each analysis was performed at least twice. The water permeates flux was determined by measuring the volume of distilled water permeate as a function of time.

3.4 Saline water

Both kinds of saline water were used: NaCl solutions prepared by using deionized water and pure NaCl (ProLabo) in the concentrations range of 0.5–3 mol NaCl.L⁻¹ and seawater from SIDI MANSOUR Sea located in the city of Sfax (Tunisia) with salt concentration at about 0.5 mol.L⁻¹. The saline water was heated in a feed tank and then circulated through the membrane module in the air-gap membrane distillation configuration process. The feed velocity of the used circulation water is 2.6 m.s⁻¹. The feed pan temperature ranges from 75 to 95°C, while keeping the cooling system side temperature constant at 5°C.

4. Results and discussion

4.1 Scanning electron microscopy (SEM)

The surface quality and morphology of the modified and unmodified ceramic microfiltration layer were examined by scanning electron microscopy. Figure 2 shows pictures of the surfaces of grafted and ungrafted microfiltration layers. The obtained photo shows that the modified surface is homogeneous without defects and was completely covered with fluoroalkylsilane (Figure 2b). We note the same that grafting
perfluorodecyltriethoxysilane on the surface of the membrane (Sand/Zirconia) led to a sharp decrease in pore size (Figure 3a and b).

4.2 Determination of pore size

The method based on N₂ adsorption and desorption was used for the determination of the pore size of the modified zirconia membrane. Figure 3 showed a type IV isotherm with hysteresis behavior associated with capillary condensation of the adsorbate in mesopores. This is done because the smaller pores became completely filled with liquid nitrogen by reducing the saturation vapor pressure, according to the Kelvin Eq. [37]. The pore diameters measured are in order of 10 nm. The decrease in the pore size of 0.22 μm before grafting to values of 10 nm after grafting clearly confirms the densification of the membrane surface shown by SEM (Figure 3).

4.3 Contact angle measurement

The hydrophobic character of the ceramic membrane was determined by measuring the contact angle of the water drop. The low contact angle of the membrane, which is approximately 18° (Figure 4), is attributed to the very hydrophilic character of the membrane due to the high density of the hydroxyl group on the surface of the membrane. After grafting, the value of contact angle increased exceeding 170°, which confirmed that the grafted membrane acquired a very hydrophobic character (Figure 4). After grafting the membrane surface, the measured contact angle increased by more than 170°. This result confirms that the grafted membrane has become very hydrophobic (Figure 5). In addition, the C8 used in this research work has a long alkyl chain of eight carbon atoms, leading to a very high increase in surface hydrophobicity.

4.4 Cross-flow filtration experiments

Water permeability measurements of the membrane were determined to assess and demonstrate the hydrophobic character of the membrane after grafting. For this, a test with grafted and ungrafted membranes was achieved. The water permeability determination of the non-grafted membrane is of the order of 720 L.h⁻¹.m⁻².bar⁻¹.
After grafting, there was a very large reduction in permeability, indeed for the microfiltration membrane grafted only $7 \text{ L.h}^{-1}.\text{m}^{-2}.\text{bar}^{-1}$ was obtained (Figure 6). So, we can say that the grafted molecules were responsible for reducing the size of the pores causing the decrease in membrane permeability, which reflected the efficiency of the graft (C8) on the zirconium oxide membrane.

4.5 Membrane distillation process of saline water

Air interval membrane distillation experiments were conducted in saline water through the prepared hydrophobic membrane. The evolution of permeate flow and
discharge rates with temperature was then determined. The feed side temperature varied from 75 to 95°C, while keeping the cooling system temperature.

### 4.6 Effects of temperature

The effects of temperature on permeate flow and release rates in the distillation of the air spacer membrane for aqueous solutions of NaCl were determined using the modified zirconium membrane microfiltration membrane at a feed rate of 2.6 m.s$^{-1}$. The temperature on the feed side varied from 75 to 95°C; keeping the cooling system temperature constant at 5°C. **Figure 6** shows the flux variations of a 1 mol.L$^{-1}$ permeate of NaCl solution examined at different temperatures. Increasing the temperature of the source solution from 75 to 95°C led to an increase of permeate flux from 76 to
155 L day$^{-1}$.m$^{-2}$ for modified zirconia membrane, in what the vapor pressure differences increase with the increase of the temperature. The effect of variable temperature on the permeates of aqueous solutions with different concentrations of NaCl was investigated using the modified zirconia membrane. The results of all these experiments are presented in Figure 7. As observed, for each temperature, the permeate flow increases with the decrease in the concentration of the NaCl solution.

4.7 Effect of concentration

In order to study the effects of feed concentration on permeate flow, several series of experiments were carried out. The experimental conditions were cooling system was maintained at 5°C, a feed velocity of 2.6 m.s$^{-1}$, and a feed temperature of 95°C. We can observe from Figure 8 that the permeate flux decreases when the feed NaCl
concentration increased from 0.5 to 3 mol.L$^{-1}$. Thus, increasing the salt concentration from 0.5 to 3 mol.L$^{-1}$ led to a decrease of permeate flux from 173 to 120 L.day$^{-1}$.m$^{-2}$ for modified MF membrane. Raoult’s Law can be used to explain these results. From Figure 8, we observed that the air-gap membrane distillation efficiency decreased over 30% when the NaCl concentration increased from 0.5 to 3 mol.L$^{-1}$. According to Raoult’s Law, the water vapor pressure over salt solutions is $P = P_0*(1 - X_{salt})$. It is concluded that the reduction of permeate flow to a percentage of 5 to 7% can be interpreted by this law. It should be noted that in all the results, the salt rejection was always greater than 99%. The rejection rate for MF-modified membrane is not modified when NaCl concentration varies.

4.8 Desalination of seawater

Seawater desalination aims to obtain fresh water for drinking. In this work, the treated seawater is taken from the sea of the region of SIDI MANSOUR Sfax (Tunisia). The measurements of the rejection rates and permeate flow were carried out by the filtered pilot used later. The feed side temperature was thus varied from 75 to 95°C, while keeping the cooling system temperature constant at 5°C. As it is shown in Figure 9, the rejection rate of NaCl is about 100% for microfiltration modified sand/zirconia membrane. These results proved that in the air-gap membrane distillation with aqueous solutions containing nonvolatile compounds such as NaCl, only water vapor is transported through the membrane.

5. Conclusion

Membrane distillation is a new technology used for desalination. This technique differs from other membrane technologies in that the driving force responsible for desalination is the difference in water vapor pressure across the membrane. In this research work, very encouraging results have been found for distillation experiments with a microfiltration modified sand/zirconia membrane. An important
influence of the feed temperature and NaCl concentration on the permeate flux was observed. At the same time, very high salt rejection rates have been found in this research with grafted sand/zirconia ceramic membranes, the rejection rate of NaCl is about 100%. The membranes for membrane distillation are hydrophobic, which allows water vapor to pass. The vapor pressure gradient is created by heating the source water. It is expected that the total costs for drinking water with membrane distillation depend on the source of the thermal energy required for the evaporation of water through the membrane. Solar energy could very much help this process in our countries, which are very sunny resulting in a reduction of energy costs. Thus, membrane distillation could become competitive relative to other processes.
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Wastewater Treatment


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