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Grafting of fluoroalkylsilanes on microfiltration Tunisian clay membrane

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Abstract

Ceramic membranes can be described by an asymmetric porous material formed by a macroporous support with successive thin layers deposited on it. Paste from Tunisian silty marls referred M11, is extruded to elaborate a porous tubular configuration used as supports. The support heated at 1190 °C, shows an average pore diameter and porosity of about 9.20 μm and 49%, respectively. The elaboration of the microfiltration layer based on Tunisian clay referred JM18, is performed by slip-casting method. The heating treatment at 900 °C leads to an average pore size of 0.18 μm. The obtained membrane was surface modified to change their hydrophilic character into hydrophobic one by the grafting of the triethoxy-1H,1H,2H,2H-perfluorodecylsilane $C_8F_{17}(CH_2)_2Si(OC_2H_5)_3$. The resulting products were investigated using Fourier transform infrared spectroscopy FTIR and thermogravimetric analysis TGA. The new surfaces were examined by water contact-angle measurements, Scanning Electron Microscopy (SEM) and the water fluxes through the grafted membranes were also measured. Results of the grafting of microfiltration membrane with fluoroalkylsilane will be given and discussed. The new hydrophobic membrane seems to be promising in the field of membrane distillation. High salt rejection rates higher than 99% were obtained for modified MF ceramic clay membrane.

Keywords: Tunisian clay; Microfiltration membrane; Grafting; Fluoroalkylsilanes

1. Introduction

In recent years, a great deal of research was devoted to the development of new types of inorganic membranes. Rapid innovations and development were already realized in this area [1]. Clay has well-known structural adsorption, rheological and thermal properties [2,3]. Research on clay as a membrane material was concentrated mainly on pillared clays [4,5]. Studies of the membranes prepared entirely from clay were just started [6,7]. Modification of the membrane material and/or the membrane surfaces has considerable influence on separation characteristics. Modification of the membrane materials surface was done to increase its hydrophilicity. Ceramic membranes were usually prepared from the metal oxides like alumina, zirconia, titania and from natural clay powder which was composed mainly of metal oxides [8–10]. These materials originally have a hydrophilic character due to the presence of the surface hydroxyl (–OH) groups, which can link very easily water molecules [11–13]. Grafting process, leading to the increase of the hydrophobic properties, can be performed by reaction between the –OH surface groups of the membrane and the ethoxy groups (O–Et) presented in the organosilane compounds [14,15]. The grafting process leads to a monomolecular layer of organosilane compound on the membrane surface [16,17]. Fluoroalkylsilanes (FAS) are the group of compounds, which can be efficiently used to create the hydrophobic character of different surfaces [18–20]. Shondelmaier et al. [16] investigated the orientation and self-assembly of different FAS. Krajewski et al. [14] has realized the grafting of ZrO_2 powder and ZrO_2 membrane by fluoroalkylsilanes and they studied the application of fluoroalkylsilanes (FAS) grafted ceramic membranes in the membrane distillation process of NaCl solutions. In the case of silane grafted clays, the organic molecule is tightly bonded onto the clay surface by the condensation between silane and surface clay membrane. Thus the release of the organic molecule into the aqueous medium was excluded. Recently, it was demonstrated that the interaction between hydrophobic molecules and the clay surfaces could be greatly enhanced by simple grafting of hydrophobic groups onto the layer surfaces [21,22].

The hydrophobic nature of the membrane prevents the passage of liquid water through the pores while allowing the

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passage of water vapour. For desalination processes like air gap membrane distillation (AGMD), the salt solution passes on the one side of the membrane at an elevated temperature, about 80 °C. At the other side of the membrane, a lower temperature obtained by cooling the condenser, creates a water vapour partial pressure difference between the two sides of the membrane and allows the evaporation through the membrane. The temperature difference produces a vapour pressure gradient, which causes water vapour to pass through the membrane and condenses on the colder surface.

The aim of this work was to prepare fluoroalkylsilanes (FAS) modified ceramic membrane by grafting microfiltration Tunisian clay membrane with triethoxy-1H,1H,2H,2H-perfluorodecylsilane molecules and to determine the properties of such modified hydrophobic ceramic membrane.

2. Experimental

2.1. Materials

Tunisian clay membrane was prepared in our laboratory from the support to the finest layer and was grafted as described earlier [23,24]. The triethoxy-1H,1H,2H,2H perfluorodecylsilane $C_8F_{17}(CH_2)_2Si(OC_2H_5)_3$ (97%) from Sigma was used. Analytical grade ethanol (99%) was purchased from Riedel-de-Haën.

2.2. Elaboration of support and microfiltration layer

Tubular supports were elaborated using silty marls powder (M11) by extrusion method. The chemical composition of these materials is shown in Table 1. The chemical analysis reveals that this kind of silty marls was essentially formed with a great amount of the silica and the calcium oxide. Plastic pastes were prepared from ceramic powder of silty marls mixed with organic additives. The mass losses are 4% for Amijel: pregelated starch, as plasticizer (Cplus 12072, cerestar), 4% for Methocel: cellulose derivative, as binder (The Dow Chemical Company), 8% for starch of corn as porosity agent (RG 03408, Cerestar) and 84% for silty marls powder. After paste extrusion, the support heated at 1190 °C, shows an average pore diameter and porosity of about 9.20 μm and 49%, respectively measured by mercury porosimetry [8]. The elaboration of the microfiltration layer was performed by slip-casting method [8]. The material used for the membrane preparation is a Tunisian clay powder (JM18) taken from the area of Sidi Bouzid (Central Tunisia). This powder was crushed for 4 h with a planetary crusher at 250 rev/min and calibrated with 50 μm. The chemical composition of the clay (JM18) is shown in Table 2. It reveals that this material was essentially formed with a large amount of silica 62.64%. For preparing a microfiltration layer with JM18, the suspended powder technique was used. A defloculated slip was obtained by mixing the masses losses: 5% for JM18 powder, 30% for polyvinyl alcohol (PVA) (12% aqueous solution) as binder and 65% for water. The heating treatment at 900 °C leads to an average pore size of 0.18 μm measured by mercury porosimetry. The water permeability determined of this microfiltration membrane is 867 $l\,h^{-1}\,m^{-2}\,bar^{-1}$.

Table 1
Mineralogical composition of silty marls (M11).

M11	Wt (%)
SiO_2	31.60
Al_2O_3	10.40
Fe_2O_3	6.50
CaO	24.20
MgO	19.90
Na_2O	2.20
K_2O	3.40
TiO_2	1.60

Table 2
Mineralogical composition of clay (JM18).

JM18	Wt (%)
SiO_2	62.60
Al_2O_3	17.10
FeO_3	8.50
MgO	0.10
Na_2O	0.30
K_2O	4.80
Mn_2O_3	0.50
SO_3	0.40
Loss on the ignition	6.20

2.3. Grafting process

Grafting of membranes was performed by the use of fluorinated silanes: triethoxy-1H,1H,2H,2H-perfluorodecylsilane. Grafting it occurs with a succession of condensation reactions between the OH groups found in the surface membrane and the Si–O–alkyl groups of the silane. To realise grafting, solutions of the triethoxy-1H,1H,2H,2H-perfluorodecylsilane were prepared in ethanol at a concentration of 10^{-2} mol l^{-1}. Prior to the chemical modification, the membranes were cleaned in an ultrasonic bath in the presence of ethanol and acetone successively for 5 min and dried in an oven at 100 °C. Samples, planar membranes as well as tubular membranes, were completely immersed in prepared solution for different times (15 min, 30 min and 60 min) at room temperature. The grafted membrane was then rinsed in ethanol and acetone successively and placed in an oven at 100 °C for 1 h.

2.4. Characterization

The FTIR spectra were obtained from KBr pellet using a Perkin- Elmer BX II spectrophotometer under transmission mode. The spectra were collected for each measurement in the spectral range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1}. Thermogravimetric analysis (TGA) was performed on a TGA2950 thermobalance. Samples were heated from 30 to 900 °C at a heating rate of 10 °C/min. The measurements of contact angles were performed at room temperature (20 °C) using a OCA 15 from Dataphysics, equipped with a CCD camera, with a resolution of 752–582 square pixels, working at an acquisition rate of 4 images per second. Collected data were processed using OCA software. Distilled water was used for measurements and planar membranes realised with clay were grafted. The drop image was recorded by video camera and digitalized. Each contact angle is the average value of 20 measurements. Grafted and ungrafetd surfaces were also characterized by Scanning Electron Microscopy (Hitachi S-4500). Water permeability was measured on grafted ceramic membranes by crossflow filtration experiments. Measurements were performed using home-made pilot plant.

3. Results and discussion

3.1. Contact angle measurements

The hydrophobic character of the resulting material was tested by measuring the contact angle of water drop. This method gives us information and a determination of the hydrophobicity of the grafted samples. Results obtained on the planar membrane are reported in Fig. 1. The low contact angle of the ungrafted membrane, results from the high hydrophilic character of the membrane surface as a consequence of the high density of the hydroxyl group on the surface of the membrane. The studied grafting times were (15, 30 and 60 min). We noticed that the value of contact angle increases weakly with the increase of grafting time.

A high efficiency of molecule triethoxy-1H,1H,2H,2H-perfluorodecylsilane and a high hydrophobicity of grafted surface is shown in Fig. 1. Values of the contact angle were in the range of 177–179 for all prepared membranes, what means that the tested membrane possessed the hydrophobic character. The high hydrophobicity of the grafted ceramic surface is illustrated in Fig. 2. We obtain non-wetting materials as we observed that there is no capillary suction of a drop of water deposited on the grafted planar membrane.

3.2. Infrared absoption spectra

Infrared spectra on each grafted or ungrafted surface membrane were measured. The infrared spectra of the ungrafted clay membrane are shown in Fig. 3a. It could be confirmed that there were hydroxyl groups in the ungrafted surface clay membrane from the band at 3100–3500 cm^{-1}. The band at 3425 cm^{-1} corresponds to the –OH stretching vibration of the adsorbed water [25]. A new band at 2978 cm^{-1} attributed to the anti-symmetric stretching of the $–CH_2$ group of the triethoxy-1H,1H,2H,2H-perfluorodecylsilane was showed in Fig. 3b, indicating the presence of silane in the grafted products. The bands at 1540 cm^{-1}, 1240 cm^{-1} and 1207 cm^{-1} corresponding respectively to the stretching vibration of the C–C, C_xF_{2x+1} and $Si–CH_2CH_2C_xF_{2x+1}$ groups. The pores size diameter and the size of the used particles for the elaborated membrane have an important influence on the amount of the grafted silanes. The grafting reaction conducted in the silane favors its entering into the clay layer.

3.3. TGA analysis

Thermogravimetric analysis (TGA) was provided as a simple method to measure the content of silane and adsorbed water. This method is based on the assumption that the dehydration and dehydroxylation reactions correspond to the

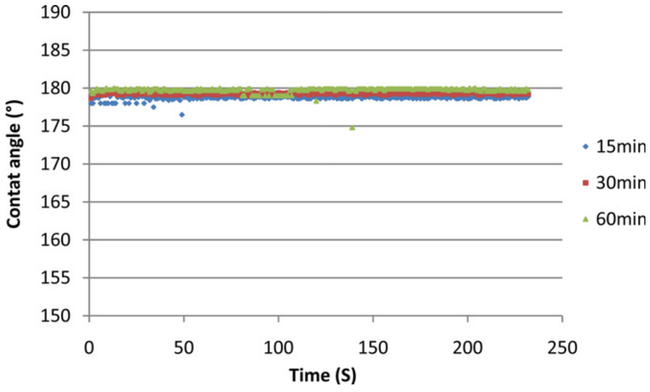

Fig. 1. Evolution of contact angle versus time of microfiltration membrane at different grafting times.

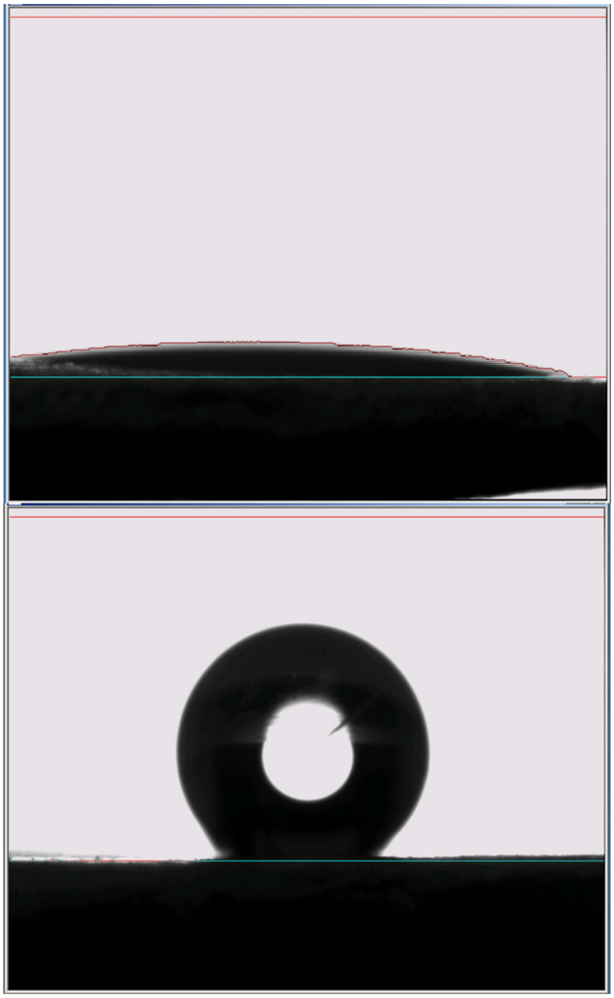

Fig. 2. Top view of a droplet of water, deposited on a membrane surface: (a) ungrafted membrane and (b) grafted microfiltration membrane.

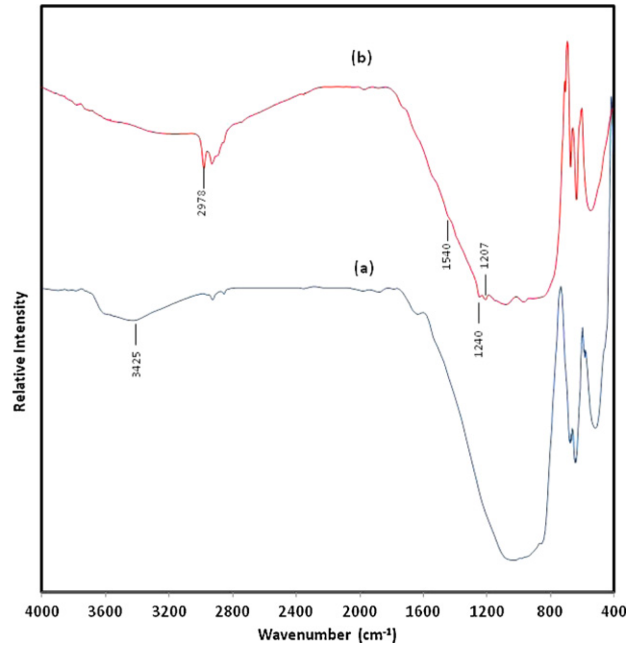

Fig. 3. Infrared spectra of (a) ungrafted membrane and (b) microfiltration grafted membrane.

two discrete mass loss steps in TG curves and they do not overlap each other. The TG curves of ungrafted membrane decreased rapidly when the decomposition temperature varied from 30 to 200 °C, resulting from the loss of water molecules for the clay membrane contained (Fig. 4a). When increasing the temperature from 200 to 900 °C, the curve was smooth with a mass loss of about 0.35%, suggesting that the membrane was very stable at high temperature. Three-stage decomposition procedure is shown in the TG curves of the grafting membrane (Fig. 4b). The initial mass loss took place between 30 and 200 °C, which was attributed to the loss of water molecules attached to the membrane. The highest mass loss in the second stage from 300 to 650 °C, results from decomposition of the grafted silane. A complete mass loss was not occurred even after heating the material up to 900 °C.

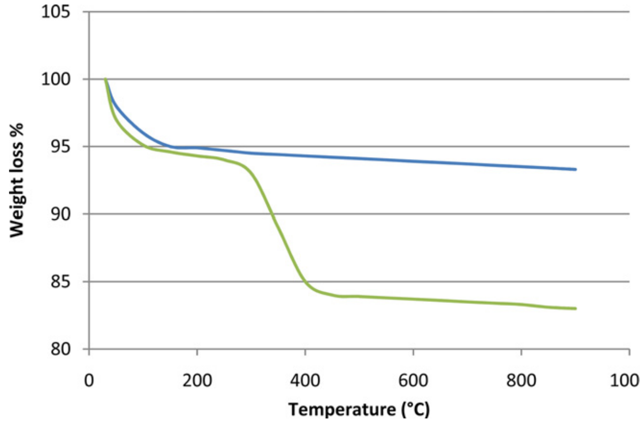

Fig. 4. TG curves of: (a) ungrafted membrane and (b) microfiltration grafted membrane.

3.4. Crossflow filtration experiments

Permeability measurements were used to test the hydrophobic character of the grafted membranes. Permeability of membranes was measured for grafted and ungrafted membranes. The ungrafted membrane exhibit a permeability of 867 l h^{-1} m^{-2} bar^{-1}. After grafting, there is a high reduction of permeability. The permeability measured for grafted microfiltration membrane was 2.7 l h^{-1} m^{-2} bar^{-1} (Fig. 5). So, we can conclude a high effect of these molecules to decrease strongly the size of pores diameters and to reduce the permeability of the membrane.

3.5. Scanning electron microscopy

The morphology, surface quality and thickness of top layer membranes were examined by scanning electron microscopy (Hitachi, S-4500). Fig. 6 shows the cross-section and the surface views of the grafted microfiltration layer. The thickness of the microfiltration layer is uniform with an average value of about 35 μm (Fig. 6b), and moreover, the surface of the grafted microfiltration layer is homogenous without defects and no microcracks (Fig. 6a). It is clear from surface image that the surface of the membrane was completely covered with fluoroalkylsilane. The top layer formed by the grafted fluoroalkylsilane present a very low thickness (in order to 2 μm). The pores become more closed and the surface more dense. This seems to affect the surface with the possibility of change in the size of pores. The experimental results of pressure drop used in Permeability measurements show that increased pressure drop occurs after modification, this way confirming our observation of SEM photograph in this figure.

3.6. Application for seawater desalination

Air gap membrane distillation (AGMD) experiments were performed for seawater desalination using prepared hydrophobic membrane. Seawater desalination aims to obtain fresh water with free salt adequate for drinking. In our work seawater treated is collected from SIDI MANSOUR Sea, located at Sfax (Tunisia). Measurements of permeate flux and rejection rates

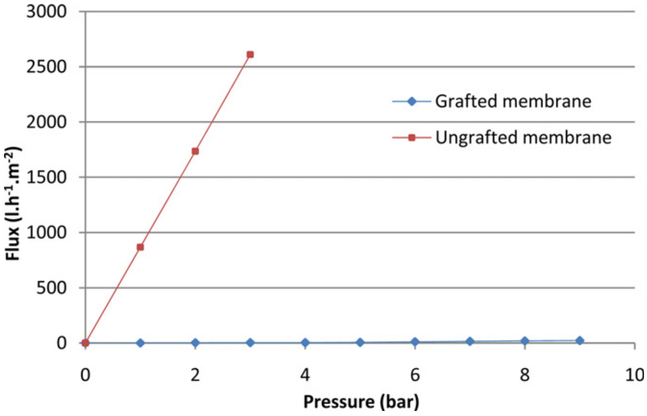

Fig. 5. Values of flux for microfiltration grafted and ungrafted membranes.

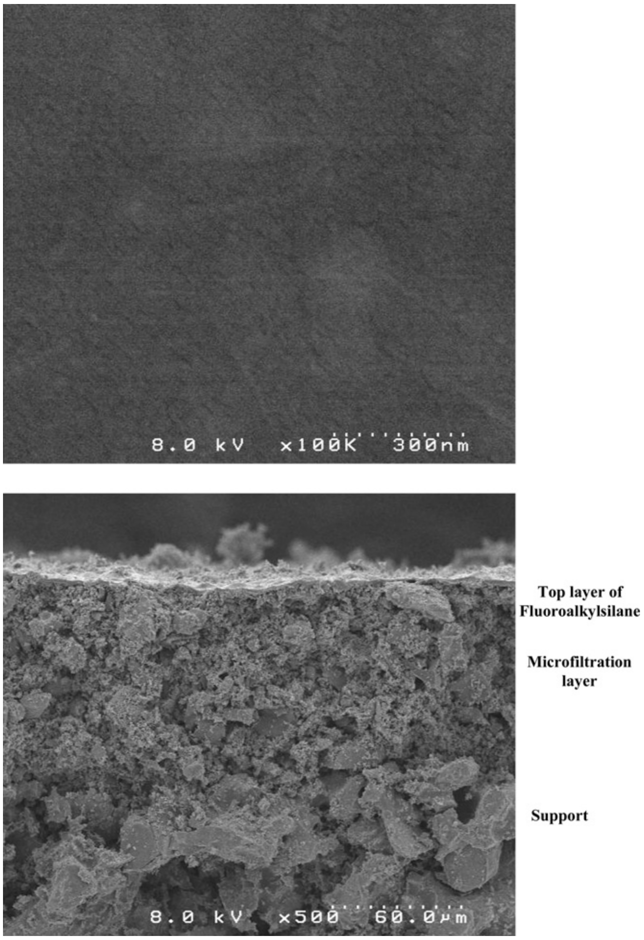

Fig. 6. SEM photographs of the grafted microfiltration clay membranes (a) surface and (b) cross-section.

were carried out by AGMD as a function of the temperature. The feed side temperature was thus varied from 75 °C to 95 °C, while keeping the cooling system temperature constant at 5 °C. It can be seen that the salt retention in AGMD process with grafted ceramic membranes is higher than 98% (Fig. 7). These results proved that in the case of AGMD with aqueous solutions containing non-volatile compounds like NaCl, only water vapour is transported through the membrane.

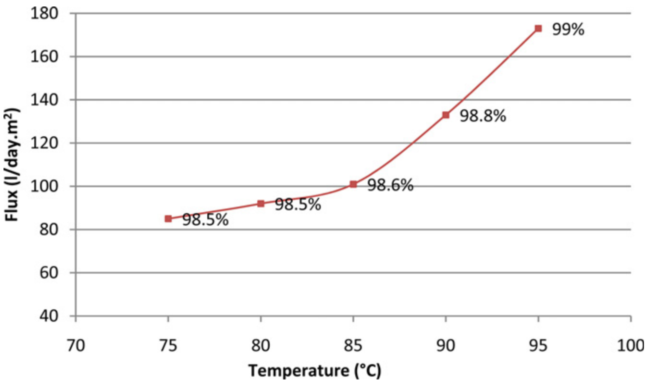

Fig. 7. Variation of the permeate flux as a function of the temperature. The values reported on the graph correspond to the rejection rates calculated for the grafted membrane after filtration of seawater.

4. Conclusion

Surface modification of the microfiltration Tunisian clay membrane by the triethoxy-1H,1H,2H,2H-perfluorodecylsilane was carried out. Ceramic membrane grafted with perfluoroalkylsilane changed the hydrophilic character into a hydrophobic one. The effect of silane treatment on the properties of the clay microfiltration layer was studied. It was proven that the presented grafted silane constitutes an ideal method for producing improved ceramic nanofiltration membranes with a decrease of the pores sizes. The data obtained with different techniques indicated a polymer grafting on the treated ceramic grains on the surface and inside the pores to form a selective barrier whose permeation flux decreases. FTIR measurement determinate the nature of chemical bonds involved in the organic layer covering the clay membrane surface. Contact-angle experiment provided important information on the wettability and the hydrophobic character of the modified surfaces. Modification of the clay surface with triethoxy-1H,1H,2H,2H-perfluorodecylsilane leads to an increase of the contact angle. High salt rejection rates were obtained in AGMD process with grafted clay ceramic membranes.

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