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Surface modification of microfiltration ceramic membrane by fluoroalkylsilane

Mouna Khemakhem, Sabeur Khemakhem, Raja Ben Amar*

Laboratoire des Sciences de Matériaux et Environnement, Faculté des Sciences de Sfax, Université de Sfax, Route de Soukra km 4, Sfax, Tunisie
Tel. +216 21603 013; Fax: +216 74274 437; email: raja.rekik@fss.rnu.tn

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ABSTRACT

Membrane separation performances regarding selectivity and permeate flux depend on the membrane texture and chemical composition of the material used for membrane elaboration. The surface properties of composite microfiltration membrane zirconium/mud of hydrocyclone laundries of phosphates with average pore diameter of 0.2 μm was chemically modified to change its hydrophilic feature into hydrophobic by grafting 1H,1H,2H,2H—perfluorodecyltriethoxysilane molecule (C_8). Observation by scanning electron microscopy showed a sharp decrease of the grafted membrane pore size. Thermogravimetric analysis was used as a technique to identify the grafted silane groups. IR analysis allowed qualitative identification of the presence of link characteristics of incorporated silanes. The determination of the contact angle on the grafted membrane surface proved the hydrophobic character since its value increases from 25° to more than 150°, respectively before and after grafting. The membrane permeability using distilled water decreased from $720\,\mathrm{L\,h^{-1}\,m^{-2}\,bar^{-1}}$ before grafting to $7\,\mathrm{L\,h^{-1}\,m^{-2}\,bar^{-1}}$ after surface modification.

Keywords: Ceramic microfiltration membrane; Grafting; Fluoroalkylsilanes; Hydrophobicity

1. Introduction

Recently, a great increase in ceramic membranes used in different applications has been observed [1–3]. The major application fields for ceramic membranes are food, biotechnology, water purification, and pharmaceutical industries. Ceramic membranes are of great interest due to their chemical inertness, porosity structure, thermal, and mechanical resistance and flux performances. However, many available inorganic membranes are made of metal oxides like alumina, titania, zirconia, Tunisian clay, and silica that are characterized by a high hydrophilic behavior due to the presence of the surface hydroxyl (–OH) groups [1–4]. The chemical modification of ceramic membranes was reported by different researchers' groups [5–13]. Rovira-Bru et al. [14] reported the modification of zirconia with terminally grafted poly(vinylpyrrolidone) (PVP). Zirconia surface was modified by a graft polymerization process consisting on silylation step followed by a surface graft polymerization of PVP. Such PVP layer

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*Corresponding author.

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can be effective in reducing the surface adsorption of water-soluble macromolecules.

The modification of ceramic membrane surface with nanometal oxide coating can be carried out by homogenous precipitation and sol–gel method [15–17]. It was found that the nano-metal oxide particles could effectively increase the ceramic membrane's performances. Li et al. [18] and Yan et al. [19] found that the nanosized alumina particles improved the antifouling performance of poly(vinylidene fluoride) membrane. The flux recovery ratio of modified membranes reached 100% after washing. Yang et al. [20] found that 2 wt.% TiO2–Polysulfone UF composite membranes had an excellent water permeability and showed some interesting properties such as hydrophilicity, good mechanical strength, and antifouling ability without changing retentions.

Some authors reported that membrane surface modification can lead to the change of the hydrophilic character of ceramic membranes into hydrophobic [5,7,8,11]. During filtration, the hydrophobic nature of the membrane prevents the passage of liquid water through the pores, while allowing the passage of gases such as vapor water. In this context, Khemakhem et al. [21,22] studied the application of membrane distillation (MD) process for seawater desalination using grafted ceramic membranes by fluoroalkylsilanes (FAS). It was found that 99% of salt was removed.

FAS are a group of compounds, which can be efficiently used to create the hydrophobic character of different surfaces [13,21,23–25]. Grafting process can be performed by the reaction between –OH surface groups of the membrane and ethoxy groups (O–Et) contained in organosilane compounds [7,22,26]. Grafting process leads to a monomolecular layer of organosilane compound on the membrane surface [23,27]. Thus, the hydrophobic character of ceramic membrane can be obtained by organosilane compounds containing hydrophobic fluorocarbon chains. Larbot et al. [7,13,28–30] reported the grafting process of different FAS on the surface of alumina, titania, zirconia, and silica membranes and used for different applications.

In previous works, we have elaborated new ceramic MF membrane based on mud of hydrocyclone laundries of phosphates as support with similar interesting properties regarding thermal, mechanical, and chemical resistances to commercial ceramic membranes based on pure oxide mineral material [31].

This work reports the results of the grafting process of FAS on MF membrane made of zirconium/mud of hydrocyclone laundries of phosphates regarding physicochemical surface properties.

2. Experimental

2.1. Reagents

Composite microfiltration (MF) membrane zirconium/mud of hydrocyclone laundries of phosphates with average pore diameters of 0.2 μm was used. The triethoxy-1H,1H,2H,2H perfluorodecylsilane $C_8F_{17}(CH_2)_2Si(OC_2H_5)_3$ (97%) was supplied from Sigma-Aldrich. This compound is characterized by a fluorocarbon chain and a siloxane head (Fig. 1). Analytical grade ethanol (95%) purchased from Chemi-Pharma, was used as solvent. All grafting processes were performed using 0.01 mol/l solution of 1H,1H,2H,2H-perfluorodecyltriethoxysilane (denoted hereafter as C_8 solution) in ethanol.

2.2. Elaboration of support and microfiltration layer

The mud of hydrocyclone laundries of phosphates chemical composition is shown in Table 1. It reveals that the major components were silica (SiO_2: 38.89%) and calcium oxide (CaO: 19.98%). The other percentage such as P_2O_5, Al_2O_3, and CO_2 are also relatively high. Tubular membrane support was elaborated by extrusion method involving the following steps described in previous paper [31] (Fig. 2):

- preparation of a plastic ceramic paste;
- shaping by extrusion;
- consolidation by thermal treatment.

The active MF layer from zirconia powder (specific area of 8 m^2) was prepared by a slip-casting process [32]. The heating treatment at 900˚C leads to an average pore size of 0.2 μm measured by mercury porosimetry.

2.3. Grafting process

The grafting method involved immersion of the ceramic membranes zirconium/mud in a 0.1 M

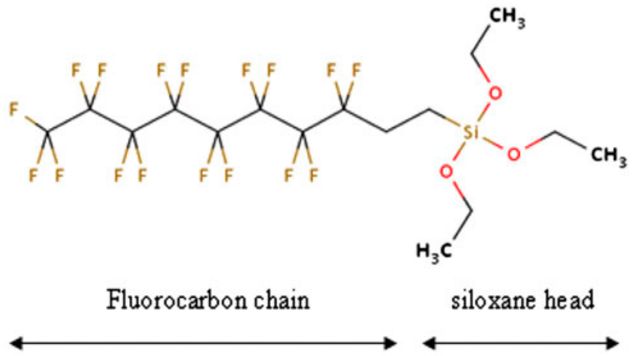

Fig. 1. Molecular structure of C8.

Table 1
Chemical analysis of the mud of the hydro cyclone laundries of phosphate powder

Elements	(wt.%)
P_2O_5	8.40
CaO	19.98
SO_4	2.47
SiO_2	38.89
Fe_2O_3	1.09
F^-	1.30
COT	1.45
Al_2O_3	6.75
MgO	1.84
CO_2	6.06
LOI*	11.77

*Loss on ignition.

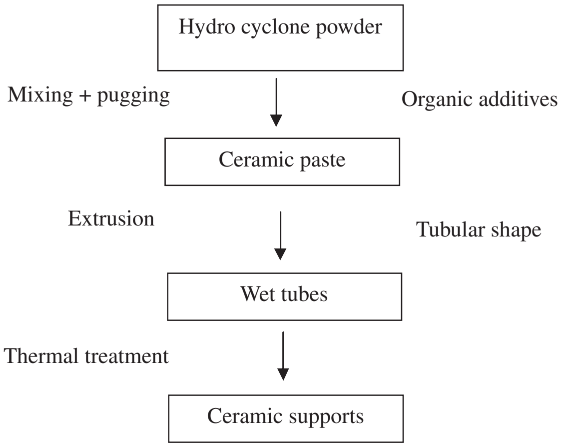

Fig. 2. Various steps of macroporous ceramic tube preparation.

ethanolic solution of $C_8F_{17}(CH_2)_2Si(OC_2H_5)_3$ at room temperature. Prior to chemical modification, the membranes were cleaned in an ultrasonic bath in presence of ethanol and acetone successively for 5 min and dried in oven at 100°C for 15 min. Grafting occurred with successive condensation reactions between OH groups found in the membrane surface and Si–O–alkyl groups of the silane. The experiments were performed for different durations (15 min, 30 min, and 1 h) at room temperature. After drying, the grafted membranes at 90°C for 1 h, membranes were rinsed with ethanol and acetone successively, and placed in oven at 100°C.

2.4. Characterization methods

The membrane morphology and the state of the surface of the grafted and nongrafted membrane were obtained using a (PHILIPS XL 30) scanning electron microscope (SEM).

Contact angle measurements were performed by the water-drop method on a KRUSS apparatus using a planar sample made for that purpose.

The FTIR spectra were obtained using IR spectrophotometer SHIMATZU IR 470. The spectra can qualitatively reveal the presence of silanes links features incorporated.

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.

Water permeability was measured on grafted ceramic membranes by cross-flow filtration experiments. The measurements were performed using home-made pilot plant.

3. Results and discussion

3.1. Scanning electron microscopy

The observation of the morphology of the modified and unmodified MF layer surface by SEM is given in Fig. 3.

The observation by SEM shows that grafting 1H, 1H,2H,2H, perfluorodecyltriéthoxysilane on the surface of membrane zirconium/mud led to a sharp decrease in pore size of the membrane surface due to the condensation of silane groups and further densification of membrane surface (Fig. 3(a) and (b)).

3.2. Thermal analysis

TGA was provided as a simple method to identify the grafted silane groups. The evolution of mass loss vs. time of grafting is shown in Fig. 4. Two inconspicuous mass loss steps in TG curves which do not overlap each other were obtained. They correspond to the dehydration and dehydroxylation reactions. Indeed, for nongrafted membrane, the entire loss was observed between 0 and 200°C, which corresponds mostly to adsorbed water or OH groups in the membrane surface. When the membrane was grafted, it was obvious that water expelled from the first grafting and the mass loss between 0 and 200°C was lower than with nongrafted membrane. This result proved that the hydrolysis of C_8F_{17} $(CH_2)_2Si$ $(OC_2H_5)_3$ molecule was close to the surface of the inorganic oxide.

The highest mass loss observed between 300 and 450°C was due to the decomposition of the grafted silane. Above 500°C, no significant mass loss occurred, which indicates complete decomposition of silane groups.

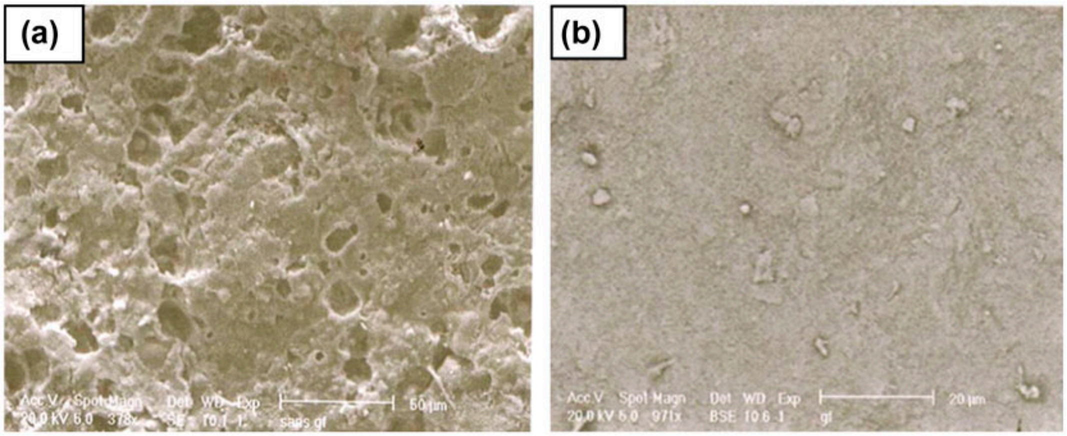

Fig. 3. **S**EM micrograph of surface of nongrafted (a) and grafted (b) membranes.

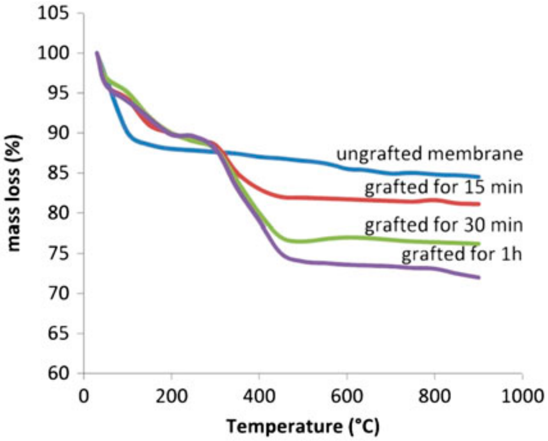

Fig. 4. TG curves of grafted and nongrafted MF membrane.

Table 2
Effect of grafting time on weight loss percentage

State of membrane	Total loss (%)
Non-grafted	17
Grafted for15 min	18.9
Grafted for 30 min	23.8
Grafted for 1 h	27.5

The mass loss increases with increasing of grafting time (Fig. 4). The percentage of weight loss was calculated and represented in Table 2.

3.3. FTIR spectrum

Fig. 5 presents the infrared spectra of grafted and nongrafted membranes. The comparison between the

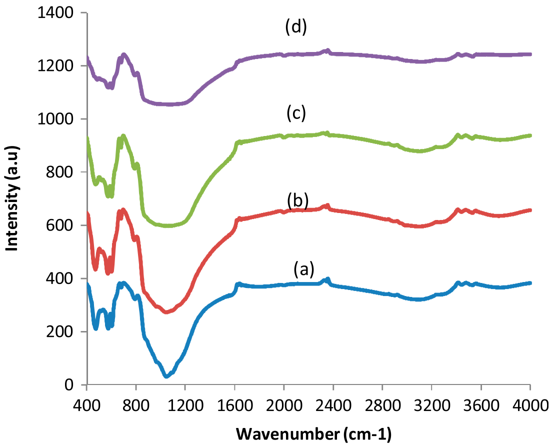

Fig 5. Infrared spectra: (a) nongrafted membrane, (b) grafted membrane for 15 min, (c) grafted membrane for 30 min, and (d) grafted membrane for 1 h.

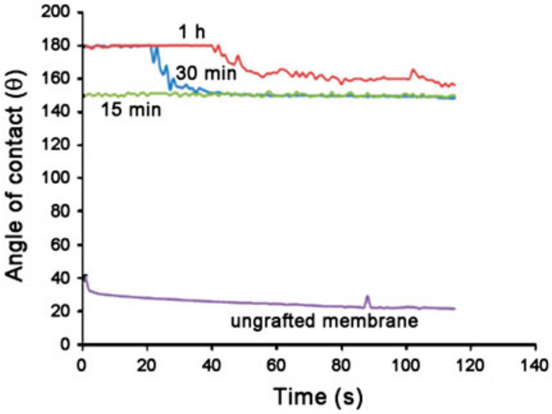

Fig. 6. Effect of grafting time on the evolution of the contact angle value.

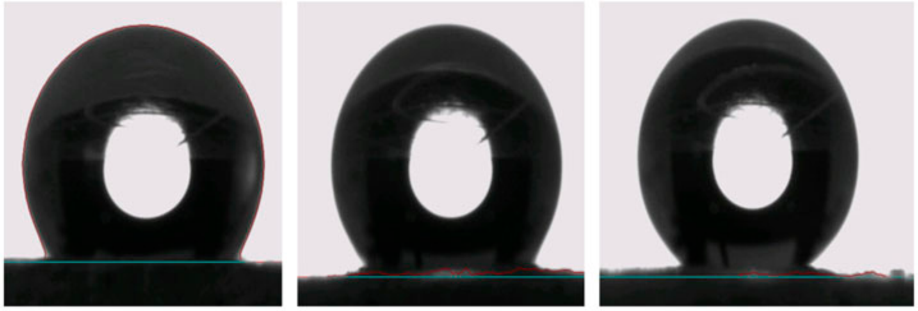
Grafting during 15 min Grafting during 30 min Grafting during 1h

Fig. 7. Evolution of contact area during different times of grafting.

two spectra shows that the presence of grafted silanes was detected. For the nongrafted spectrum, the band at 1,032 cm^{-1} is attributable to the Si–O–Si [33]. After grafting, this absorption band became wider between 900 and 1,200 cm^{-1}, which indicated that the number of Si–O–Si band increased. The absorption band widened more and more with the grafting time, which revealed the efficiency of grafting time variation. Longer the grafting duration, more the silane groups grafted.

3.4. Contact angle measurement

The hydrophobic character of the ceramic membrane was demonstrated by measuring the contact angle of water drop. Results obtained on the planar membrane are reported in Fig. 6. The low contact angle of about 25° for the nongrafted membrane is attributed to the high hydrophilic character of the membrane surface characterized by high hydroxyl group density. After grafting, the value of contact angle became very high exceeding 150°, which confirmed that the grafted membrane got a hydrophobic character.

Fig. 7 shows that the surface of contact between the drop and the membrane decreased with increasing grafting time.

So, it can be concluded that grafting time is important to reach highest hydrophobicity for ceramic membranes.

3.5. Determination of membrane permeability

The membrane permeability (L_p) can be determined using the variation of distilled water flux (J_w) with transmembrane pressure (ΔP) following the Darcy's law:

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

where

$$\Delta P = [(P_{\text{inlet}} + P_{\text{outlet}})/2 - P_{\text{f}}] \tag{2}$$

P_{inlet} = inlet pressure; P_{outlet} = outlet pressure; P_{f} = filtrate pressure.

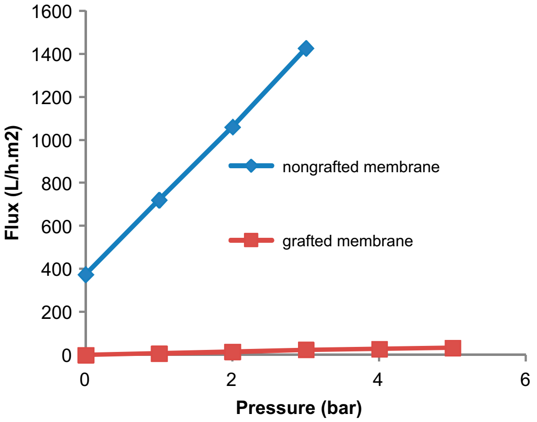

Fig. 8. Evolution of the permeate flux (L/hm^2) of the grafted and nongrafted membrane.

The nongrafted membrane exhibited a permeability of 720 $\text{L h}^{-1} \text{m}^{-2} \text{bar}^{-1}$. After grafting, a severe reduction of water permeability was obtained. The permeability measured for grafted microfiltration membrane is 7 $\text{L h}^{-1} \text{m}^{-2} \text{bar}^{-1}$ (Fig. 8). The sharp decrease of the membrane permeability can be attributed to both decrease of pores size and hydrophobic character due to C_8 grafting.

4. Conclusion

The hydrophilic character of the ceramic membranes zirconium/mud of hydrocyclone laundries of phosphates can be changed into hydrophobic by grafting C_8 compound on the membrane surface.

Moreover, the high fluorinated silanes efficiency in the obtaining of nonwetting materials was determined and the importance of grafting time to increase the hydrophobicity of grafted samples was demonstrated. Grafted membrane seems to be suitable for membrane separation processes, which need hydrophobic membrane character such as gas separation, organics/water mixtures separation, and desalination by MD.

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