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Membrane distillation properties of TiO_2 ceramic membranes modified by perfluoroalkylsilanes

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ABSTRACT

The tubular and planar TiO_2 ceramic membranes were modified by grafting with perfluoroalkylsilanes (PFAS) molecules. Two types of PFAS were used for grafting process: 1H,1H,2H,2H-perfluorooctyltriethoxysilane (C6) and 1H,1H,2H,2H-perfluorotetradecyltriethoxysilane (C12). Studies showed that hydrophilic surface of titania ceramic membranes can be efficiently modified as a results of the proposed grafting method. Grafting efficiency of the tubular membranes was determined by measurement of liquid water entry pressure (LEP_w), whereas grafting efficiency of planar membranes was verified by contact angle measurement. The contact angle values of the planar membranes are 130 and 140° for grafting with C6 and C12, respectively. The LEP_w of the tubular membranes increased from 2 bar to 10 bar after modification by C12, whereas the LEP_w values were constant at 2 bar when TiO_2 membrane was modified by C6 molecules. It was found that water contact angle, LEP_w, and water flux in the membrane distillation (MD) process essentially depend on the time of grafting and the type of PFAS used. Retention coefficients for both membranes are very high, close to unity. The results were additionally analyzed using chemometric simplex method, this resulted in determining the optimum time of grafting. For the membrane grafted by C6, the optimum time according to simplex method was equal to 26 h (flux 4055 [$g\,h^{-1}\,m^{-2}$]), whereas for a membrane grafted by C12 was 17 h (flux 4535 [$g\,h^{-1}\,m^{-2}$]). The highest fluxes of permeate in MD were observed for the optimum times of grafting.

Keywords: Ceramic membranes; Surface modification; Perfluoroalkylsilanes; Simplex method

1. Introduction

The ceramic membranes are chemically, thermally, and mechanically stable. Therefore, they are ideal for many applications in the chemical and pharmaceutical industry, as well as in water and wastewater processing [1,2].

The starting materials for ceramic membranes preparation can be titania, zirconia, and alumina oxides. The above mentioned materials are of hydrophilic character, which is the consequence of the presence of hydroxyl groups on the membrane surface. The modification of the surface by grafting can

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change a surface character from hydrophilic into hydrophobic one, resulting in an alteration of the selective and transport properties [3–19]. Hydrophobic terminated compounds with reactive grouping (methoxy, ethoxy, or active chlorine) must be used for the surface modification process. These reactive groups react with hydroxyl groups on the membrane surface, thus creating stable covalent bonds. The hydrophobic parts of the molecules form a monolayer brush on the ceramics surface.

The early research on the surface modification of ceramic membranes has been conducted by Okubo and Inoue [6]. They performed modification of SiO_2 membrane by using tetraethoxysilane (TEOS). The researchers examined selectivity of the modified membrane in the separation of helium–oxygen gas mixture. They have observed an increase in selectivity coefficient of modified membrane for helium in comparison with unmodified membrane [6].

Miller and Koros [7] have been working on the chemical modification of γ–Al_2O_3 membrane with average pore size of 4 nm by using tridecafluoro-1,1,2,2-tetrahydrooctyl-1-trichlorosilane (TDFS). The permeability measurements indicated that the short-term modification (i.e. during 24 h) produces a membrane that has still an acceptable amount of surface flow, while the membrane modified for two weeks shows a hindered surface transport [7].

Paterson et al. [8,9] modified ZrO_2 and TiO_2 membranes by phosphoric and alkylphosporic acids, this resulted in an increased hydrophobicity of membranes. The modified membranes were used in protein ultrafiltration of BSA (Bovine serum albumin) [8]. At pH 7, both untreated titania membrane and phosphoric acid treated membrane possessed almost equal charge, but rejection and permeate flux for the phosphorylated titania membrane were much higher. Modified membranes have been also utilized for various gas permeation tests, e.g. methane, ethane, propane, hydrogen, nitrogen, and carbon dioxide. Modified membranes displayed both higher permeability and higher selectivity coefficient for carbon dioxide separation [9].

Alumina membranes were modified by the same research group using trichloro-octadecyl silane (ODS) [10] and phenyltriethoxysilane to improve separation of CO_2 from N_2 [11]. The research shows that the permeability characteristics of the membrane are changed by the rearrangement of the octadecyl chains on the alumina surface. The mechanism of modification was presumed to be due to the free movement of the unbounded parts octadecyl of the silane chains, which resulted in a partial blocking of the membrane pores. Authors highlighted this phenomenon as a unique example of self-fouling [11].

Castro et al. [12–14] demonstrated that the permeability features of silica membranes could be altered by graft polymerization of PVP onto the membrane pore surface. It was found that the PVP-silica membranes exhibit a hydraulic permeability dependent on the polarity of the used solvent [12,13]. PVP brush layers are effective in reducing surface adsorption of water-soluble macromolecules and thus, suitable for the protein adsorption reduction. Recent studies of Castro et al. [14] have also reported that low-temperature plasma graft polymerization of N-vinyl-2-pyrrolidone (NVP) onto poly(ether sulfone) membranes reduces membrane fouling during a filtration of bovine serum albumin, confirming the relevance of PVP for protein adsorption reduction [14].

Larbot and others [1–5][15,16] performed the most extensive studies on the ceramic membrane modification. ZrO_2 and γ-Al_2O_3 membranes have been modified by various alkyl siloxanes: $C_6F_{13}C_2H_4Si(OMe)_3$, $C_8F_{17}C_2H_4Si(OEt)_3$, $Me_2Si(OEt)_2$, $MeSi(OEt)_3$, and $Me_2Si(OEt)_2$ [15,17], where OMe and OEt denotes methoxy and ethoxy groups, respectively. The modification has led to an effective hydrophobization of the ceramic surface. The modified membranes were examined in pervaporation of various water–organic liquid mixtures [2] as well as in membrane distillation (MD) process for seawater desalination [1,3,4].

Li et al. [18,19] prepared alumina hollow fiber membranes [18] and yttria-stabilized zirconia (YSZ) hollow fiber membranes [19] and modified them with 1H,1H,2H,2H-perfluorooctylethoxysilane (FAS). The gas permeation results showed slight decrease in gas permeability of the modified membranes in contact with nitrogen due to the additional resistance from a FAS layer formed on the membrane surface [18]. The membranes were found to be thermally stable in temperatures up to 250°C. These membranes were also chemically stable, showing no changes in their hydrophobicity properties after being in contact with hexane for 96 h.

In the literature, there are only few papers on the characteristics of the structure of hydrophobic layer formed on the ceramic membrane surface. Shondelmaier et al. [20] tried to explain the PFAS molecules orientation and self-organization on modified surfaces by using X-ray photoelectron spectroscopy and X-ray absorption near edge spectroscopy techniques. He suggested that PFAS molecules form a monolayer brush which is strongly bonded and perpendicular to the substrate surface [20].

This work reports the results of the grafting process of PFAS compounds on the planar as well as on tubular titania membranes. The aim of this work was to determine the efficiency of surface modifica-

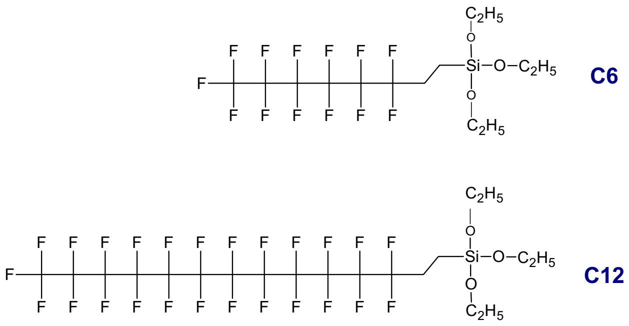

Fig. 1. C6 and C12 (PFAS) chemical formula.

tion of TiO_2 ceramic tubular membranes, subsequently, applied in MD of aqueous sodium chloride solution.

The grafting was performed by using two types of perfluoralkylsilanes compounds (Fig. 1): $C_6F_{13}C_2H_4Si(OEt)_3$ (denoted as C6) and $C_{12}F_{25}C_2H_4Si(OEt)_3$ (denoted as C12).

Grafting leads to the increased hydrophobicity of the membrane surface. Therefore, the hydrophobicity of modified membranes was assessed by the water contact angle and liquid entry pressure for water (LEP_w).

Additionally, the optimization of the grafting process by applying the simplex chemometric method was proposed and discussed.

2. Experimental part

2.1. Membranes

In this study, TiO_2 tubular ceramic membranes were applied with 10/5 mm outer/inner diameter and 15 mm in length as well as 3 mm thick planar membranes with 47 mm in diameter. Both types of membranes were provided by TAMI Industries (France). The tubular membranes with a cut-off of 300kD and planar ones with a cut-off of 1kD were used.

The tubular membranes modified by C6 and C12 were denoted as Ti-tC6 and Ti-tC12, respectively, whereas planar membranes modified by C6 and C12 were denoted as Ti-pC6 and Ti-pC12.

2.2. Grafting process

0.05 M grafting solutions were prepared by dissolving the appropriate amount of C6 and C12 molecules (Apollo Scientific, UK) in chloroform (Carlo Elba, France) under an ambient atmosphere of argon. Grafting process and preparation of C6 and C12 solutions require an ambient atmosphere to avoid the polycondensation of PFAS in the presence of traces of moisture from air. Modification was carried out at room temperature.

Before grafting process, membranes were cleaned by a sequential rinsing in acetone, ethanol, and distilled water for 10 min in each solvent. The purified membranes were subsequently dried at 110°C for about 12 h.

The single stage of a membrane modification consisted of the following steps:

- grafting of membranes by dipping in a grafting solution for 1–6 h,
- sequential rinsing (in acetone, ethanol, and distilled water) followed by drying of grafted membranes (12 h at 110°C). This step allowed to remove unbonded PFAS molecules from the membrane surface and pores,
- determination of LEP_w value followed by rinsing with water and drying for 2–3 h at 110°C, and
- MD process of 0.5 M NaCl (4–6 h) followed by rinsing in water and drying for 12 h at 110°C.

The unit sequence for planar membranes modification consisted of the following steps: grafting (1–4 h), sequential rinsing (in acetone, ethanol, and distilled water), drying (12 h at 110°C), and the angle contact measurements.

The total grafting time was 31.5 h for Ti-tC6 and 37 h for the other membranes (Ti-tC12, Ti-pC6, and Ti-pC12).

2.3. LEP_W measurements

LEP_w measurement is a method used to determine the degree of hydrophobicity of the porous membranes. As a result of grafting, the hydrophobic layer is created and the value of LEP_w increases. LEP_w is defined as the pressure, at which a liquid penetrates the pores and is transported through the hydrophobic membrane. Pressure is related to the surface tension, contact angle on membrane surface, and pore radius, which can be expressed by the Laplace—Young Eq. (1) [21].

$$\Delta P = \frac{2\gamma_L}{r}\cos\theta_{ef} \tag{1}$$

where ΔP is the pressure difference at the liquid—gas interface, γ_L is the surface tension of liquid, r is the radius of the sphere, and θ_{ef} is the effective contact angle.

Fig. 2 illustrates the scheme of LEP_w measurement equipment. Compressed nitrogen was used to generate pressure that was controlled by a precise pressure

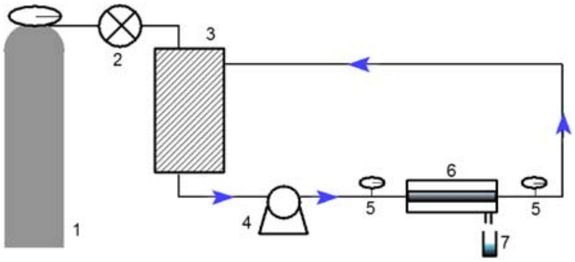

Fig. 2. Scheme of the laboratory LEP setup (1: compressed nitrogen, 2: pressure gage, 3: thermostated tank with water, 4: pump, 5: valves, 6: membrane module, and 7: trap).

regulator. The applied pressure was measured with a digital pressure gage (range 0–12 bar). At the beginning of the experiment, a dry membrane was placed inside the module and the flow of water in the membrane lumen was started to circulate. The pressure difference has been increasing slowly and stepwise by adjusting the pressure regulator. The pressure value (ΔP) at which the first drop of water appears on the permeate side of a given membrane corresponds to the LEP_w value.

2.4. Contact angle

Contact angle measurement is another method used to evaluate the degree of hydrophobicity. Within this study, the Eq. (1) was used to correlate LEP_w values and contact angle values for tubular membranes. Moreover, with a help of Eq. (1), it was also possible to compare the grafting efficiency of both types of membranes.

Contact angle measurements were used to evaluate the effects of the surface modification and the hydrophilic/hydrophobic properties of planar membranes. The measurements were carried out by taking a photograph of a water drop on the membrane surface using digital camera. Subsequently, with the aid of a software (ImageJ, NIH—freeware version) allowing an edition of images, the value of contact angle was determined. The measurement accuracy was $\pm 2^\circ$.

2.5. Membrane distillation

The membrane distillation is a separation process, in which hydrophobic porous membranes are used. During the process, the hydrophobic membrane should not be wetted by feed solution. In this process, high temperature feed solution is in direct contact with one membrane surface, whereas the permeate can be received in various modes [1,3,4,22–25]. Difference of the chemical potential induced by temperature difference between feed and permeate is the driving force in MD.

According to the approved transport model [1,2,26], the transport of solvent vapors during MD is proportional to the difference of water vapor partial pressures between feed and permeate liquids. It can be calculated on the basis of the following equation:

$$J = K(p_f - p_p) \tag{2}$$

where K is the transfer coefficient ($kg\,m^{-2}s^{-1}Pa^{-1}$), p_f is the partial vapor pressure of water in feed phase, p_p is the partial vapor pressure of water in permeate phase, and K is a mass transfer coefficient, which is a function of temperature, pressure, and membrane structure. The feed partial pressure of water $p_{f,}$ and the permeate partial pressure of water p_p can be calculated from Antoine's Equation [1,2]:

$$p_i = exp\left(A - \frac{B}{C+T}\right) \quad i = f, p \tag{3}$$

Factors A, B, and C in Antoine's equation are characteristics of a particular solvent and in the case of water they are given as follows: $A = 23.1964$, $B = 3816.44$, and $C = 46.13$ [1].

The temperature of the feed solution decreases at the boundary layer of the membrane as a result of the heat loss related to water vaporization, whereas on the permeate side the permeate temperature increases due to the energy release upon vapor condensation. This phenomenon is defined as the temperature polarization and is responsible for the driving force diminution in MD process influencing the transport properties of a given membrane [27].

In this study, NaCl solution of 0.5 M has been prepared by using distilled water and pure NaCl (ProLabo, France). Salt rejection measurements have been carried out by using ion chromatograph (Dionex DX-100 Ion Chromatograph).

The MD process was conducted in an air gap membrane distillation (AGMD) mode presented schematically in (Fig. 3). Ti-tC6 and Ti-tC12 tubular

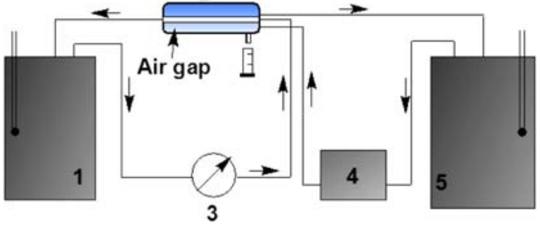

Fig. 3. Setup of air-gap membrane distillation (1: thermostated feed tank, 2: thermostated membrane module, 3: pump, 4: cooling system, and 5: thermostat).

membranes grafted for a given period of time were tested at feed temperature of 90°C and permeate temperature of 5°C. Additionally, the process of MD for Ti-tC6 grafted for 3.5 h was performed at feed temperatures: 70, 80, and 90°C, while keeping the permeate temperature at 5°C. The permeate flux was measured by determining the mass of liquid collected during experiments lasting for 3–5 h. The permeate flux was measured after running the apparatus for at least 1 h. This time was needed to attain the stationary state within the system. After each experiment, the membrane was washed several times in distilled water to prevent crystallization of NaCl on the surface and in the pores of the membrane.

3. Results and disscusion

3.1. Tubular membranes

The influence of grafting time by C6 and C12 solutions on transport properties in the MD process is presented in Fig. 4. Fig. 4 displays also numerical study of LEP$_w$ values measured after the each stage of grafting.

The determined LEP$_w$ values for Ti-tC12 membrane increased with increase of the total grafting time, reaching a plateau at 5 bar between 17 and 25 h of grafting, and finally reaching value of 10 bar for a grafting time longer than 27 h. In case of the Ti-tC6 membrane, LEP$_w$ value was equal to 2 bar and did not depend on the grafting time. The LEP$_w$ values for nongrafted membranes were equal to 0 bar.

The results presented in Fig. 4 suggest that after grafting time longer than 20 h, the flux value for Ti-tC6 is practically constant and equals 3,800 $(\mathrm{g\,m^{-2}\,h^{-1}})$. It can be stated that this period of time is sufficient to cover all active sites on membrane surface by C6 molecules. In case of membrane grafted by C12, for grafting time longer than 20 h a slight decrease in flux is observed, which might suggest that longer fluorocarbon chains have blocked the transfer of water molecules through membrane pores. The observed increase in the flux for the grafting time shorter than 20 h can be explained by heterogeneous distribution of PFAS molecules on the surface and inside the membrane pores.

The influence of feed temperature (70, 80, and 90° C) on the transport properties of the membrane grafted by C6 has also been examined. With increasing temperature difference between feed and permeate, the flux of water increases. The driving force expressed by a pressure difference was calculated according to Eq. (3). Fig. 5 presents the variation of the average permeate flux with the driving force in MD process.

The permeate flux was increasing with increase in driving force (p_f–p_p); however, the relation was nonlinear. This indicates the importance of the possible temperature polarization during MD process.

The obtained results for NaCl rejection are presented in Table 1. The rejection coefficient (R) was calculated according to Eq. (4).

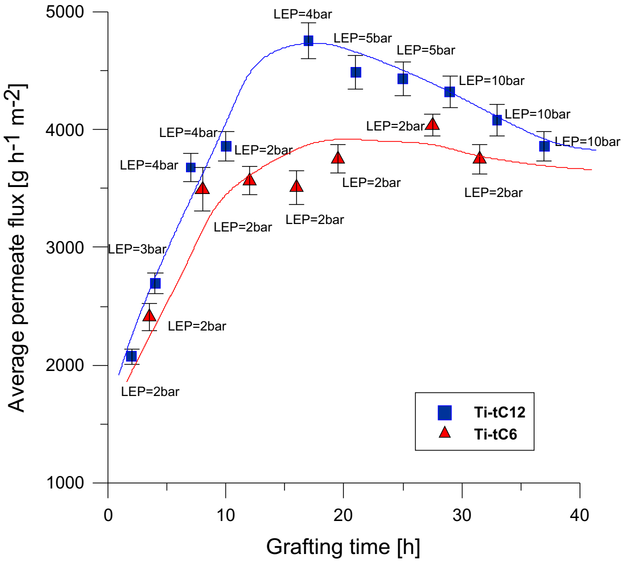

Fig. 4. Influence of grafting time for efficiency and transport properties (tubular membranes). Conditions of AGMD process: feed temperature 90°C and permeate temperature 5°C.

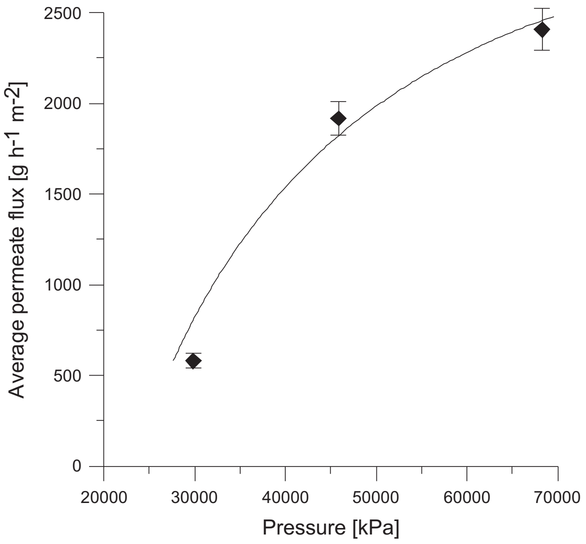

Fig. 5. Permeate flux vs. pressure difference in membrane distillation process (Ti-tC6: tubular membrane grafted by C6). Conditions of membrane distillation process: feed temperatures 70, 80, and 90°C and permeate temperature 5°C.

Table 1
NaCl retention coefficient in the membrane distillation process for Ti-tC6 and Ti-tC12 membranes

Temperature feed/permeate (℃)	Retention coefficient R_{NaCl} (%)	LEP (bar)	Total grafting time (h)	Flux (g h^{-1} m^{-2}]
Ti-tC6 membrane				
70/5	92.3	2	3.5	560
80/5	99.5	2	3.5	1,917
90/5	99.8	2	3.5	2,406
Ti-tC12 membrane				
90/ 5	97.2	2	2	2,072
	95.8	3	4	2,694
	94.0	4	7	3,677
	92.2	4	10	3,858
	92.3	5	17	4,755

$$R_{NaCl} = 1 - \frac{C_p}{C_f} [\%] \tag{4}$$

C_p is the concentration of NaCl in permeate and C_f is the concentration of NaCl in feed.

In the MD process, a high level of NaCl rejection was observed. NaCl retention coefficient in the MD process was in a range from 92.2 to 99.8%, depending on the total grafting time and the temperature difference between feed and permeate.

According to the Eq. (1) and experimental LEP_w values for tubular membranes, the theoretical contact angle values for tubular membranes (Ti-tC6 and Ti-tC12) were also calculated (Fig. 6). Certainly, tubular membranes grafted by C12 were characterized by higher values of contact angle. After modification with C6 and C12 molecules, the contact angle values were equal to 94° (Ti-tC6) and 110° (Ti-tC12), respectively.

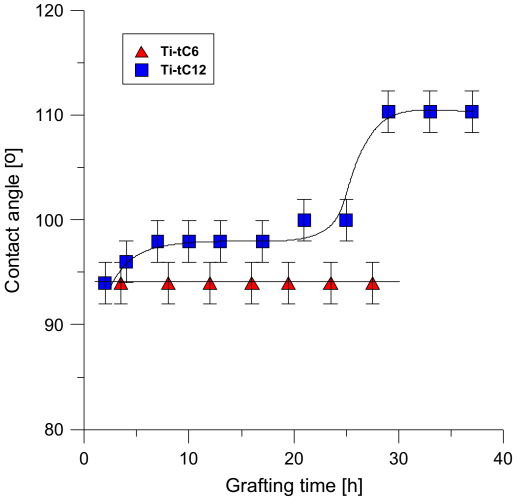

Fig. 6. The efficiency of tubular membranes grafting by PFAS. Comparison of calculated contact angle for Ti-tC6 and Ti-tC12 membranes.

3.2. Planar membranes modification

Fig. 7 presents the photography of a water drop placed on the surface of the unmodified TiO_2 membrane (Fig. 7(A)) and the membrane modified by C12 solution (Fig. 7(B)). It can be observed that unmodified TiO_2 is hydrophilic, whereas the modified surface shows hydrophobic properties. In order to determine the grafting efficiency, the contact angle was measured. The contact angle values for planar membranes as a function of grafting time are presented in Fig. 8.

It can be seen that for the planar membranes modified by C6 and C12 solutions certain regularity could be observed. During first 4 h of modification, the contact angle values remained at constant value of 107° and 127° for the membrane modified by C6 and C12, respectively. Subsequently, the value of the contact angle increased sharply to approximately 132° (C6) and 143° (C12) between 4 and 10 h of grafting. For a grafting time longer than 10 h, the value of contact angle was stabilized at 130° and 140° for Ti-pC6 and Ti-pC12 membranes, respectively. Higher values of

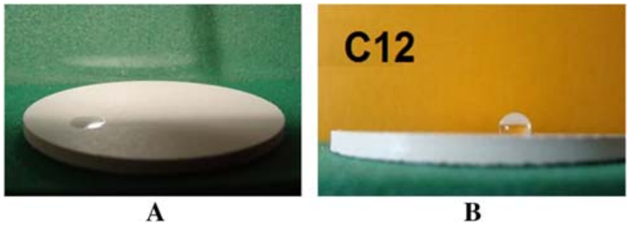

Fig. 7. Behavior of water drop on a surface of TiO_2 ceramic membranes: (A) unmodified membrane and (B) membrane modified by C12 compounds.

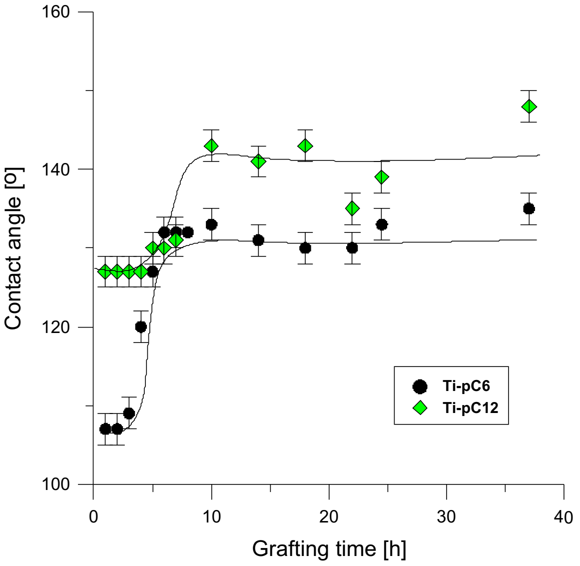

Fig. 8. Influence of grafting time on contact angle (planar membranes). Ti-pC6: planar membrane grafted by C6 and Ti-pC12: planar membrane grafted by C12.

contact angle were observed during modification of membrane grafted by C12 solution rather than for membrane modified by C6. This can be explained by the fact that C12 molecules possess longer hydrophilic chains which covered the surface to much higher extent.

3.3. Optimization of grafting by simplex method

The original simplex concept was derived by Box and Wilson who combined response surface methodology and hill-climbing techniques to produce an algorithm capable of varying simultaneously many factors and arriving at the optimum level of response. That technique was known as “evolutionary operation.” Nelder and Mead provided a simple yet powerful modification and the original simplex method, and at this time, the method has been used in a wide variety of applications [28–32].

The simplex method is a sequential method based on a systematic search for response surface and selection of new parameters, and then repeating this sequence to obtain the parameters producing the optimal value of the objective function [28–34].

The variable inputs, upon which the response depends, are known as factors. A simplex figure is a geometric figure having one vertex more than the number of factors. Examples of simplexes include a line segment on a line (for one factor), a triangle on a plane (for two factors), and a tetrahedron in three-dimensional space (for three factors). In a two-dimensional space, a basic simplex is a triangle formed by connecting the three points (Fig. 9)

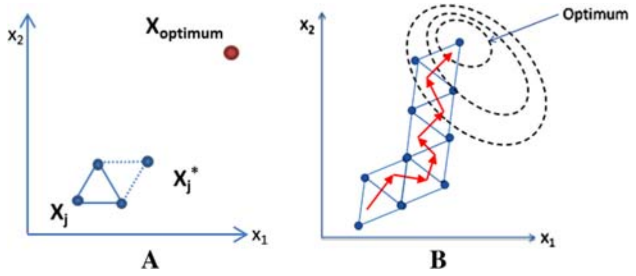

Fig. 9. Two-dimensional simplex: (A) determining a new set of optimization parameters (new simplex point) and (B) simplex movement to the optimum area.

The simplex algorithm consists of the general rule that the least fit trial value in the basic simplex is rejected. Subsequently, a new set of optimization parameters is calculated. The value of this new set of parameters (Xj*) is symmetrical to the value of rejected factor (Fig. 9(A)). Subsequently, this leads to a new least favorable response in the simplex which, in turn, leads to another new trial. The simplex expands in a direction of the most favorable optimal response function (Fig. 9(B)).

The grafting results were analyzed by using simplex method to determine the optimal grafting time. In this optimization, the permeate flux in MD process was chosen as an objective function, whereas the grafting time was chosen as a control variable.

The results of simplex modification as well as comparison with experimental date are presented in Fig. 10(A). In Fig. 10(B), the movement of simplex toward the optimum grafting time for Ti-tC12 membranes is presented. It can be seen that using a simplex algorithm, the optimum time of around 17 h was found to be within 10–20 approximation steps. To verify if this is a local or global optimum, the calculations were continued for the variables outside the optimum range (steps 20–35). It turned out that the simplex moved back to the value of around 17 h as the most optimal grafting time for C12 molecules, providing flux of ca. 4,520 $\mathrm{g\,h^{-1}\,m^{-2}}$. This time of grafting fits well the experimental value found for this system (Fig. 10(A))

On the other hand, the time of grafting determined by simplex optimization for TiO_2-tC6 membrane was equal to 26 h. The flux value for 26 h of modification was equal to 4,055 ($\mathrm{g\,h^{-1}\,m^{-2}}$). The experimental maximum flux for Ti-tC6 membrane was equal to 4,040 ($\mathrm{g\,h^{-1}\,m^{-2}}$) after 27.5 h of grafting. The values

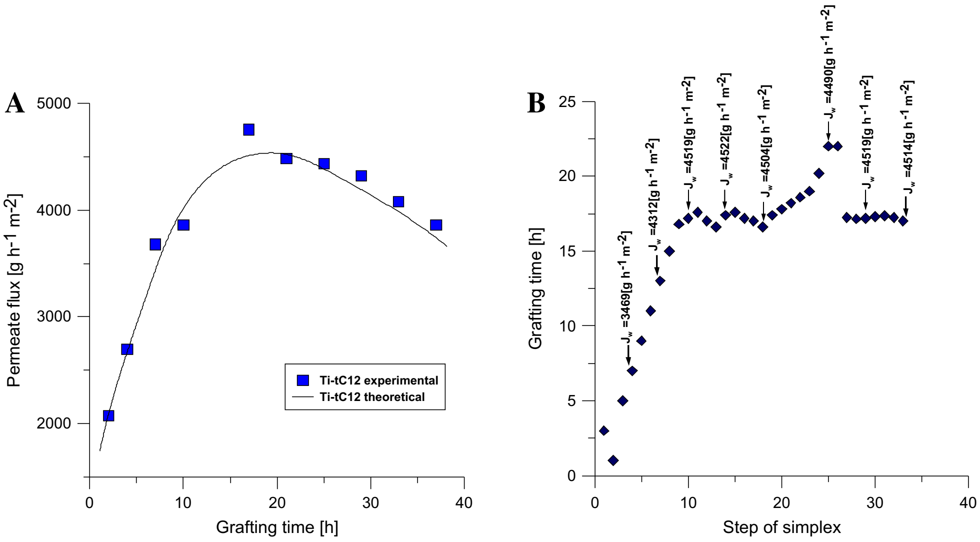

Fig. 10. The results of simplex optimization. (A) Comparison of theoretical and experimental permeate flux vs. grafting time and (B) The movement of simplex.

obtained from the experiment and determined by the simplex method were quite similar.

4. Conclusions

According to the obtained results, modified membranes show hydrophobic character suggesting various future applications of such membranes, e.g. for the removal of volatile products from bioreactors [35], water desalination [22], or concentration of aqueous solutions (fruit juice and sugar solution) [23].

The following conclusions can be drawn out from the obtained results:

- The efficient change of membrane character from hydrophilic to hydrophobic was proven.
- The length of hydrophobic PFAS molecules has an important impact on the resulting hydrophobic character of modified membranes.
- Membrane separation and transport properties in the MD depend considerably on grafting parameters (grafting time and type of grafting compound). The tubular membrane grafted by C12 solution displays both higher permeability and higher value of LEP_w than the membrane grafted by C6 compound. This is related with the efficiency of grafting process. The level of NaCl rejection in MD process was high with values ranging from 92 to 99.8%. The increase in feed temperature causes the increase in permeate flux values during the MD process (AGMD).
- The planar membrane modified by C12 solution is characterized by a higher value of contact angle (140°) than the membrane modified by C6 solution (130°).
- The simplex method can be efficiently used to estimate the optimal conditions of grafting.

Acknowledgments

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List of abbreviations and symbols

AFM — atomic force microscopy
AGMD — air gap membrane distillation
B — cylindrical pore factor
BSA — bovine serum albumin
C6 — 1H,1H,2H,2H-perfluorooctyltriethoxysilane
C12 — 1H,1H,2H,2H-perfluorotetradecyltriethohysilane
EVOP — evolutionary operation
J — flux
K — transfer coefficient
LEP_w — liquid entry pressure for water
MD — membrane distillation

NVP — N-vinyl-2-pyrrolidone
p_f — partial vapor pressure of water in feed
p_p — partial vapor pressure of water in permeate
PFAS — perfluoralkylsilane
PVP — poly(vinylpyrrolidone)
PVPc — poly(vinyl acetate)
q_m — heat transfer coefficient
r — radius of the sphere
R_{NaCl} — rejection coefficient for sodium chloride
T_f — feed solution temperature
T_p — permeate solution temperature
TDFS — tridecafluoro-1,1,2,2-tetrahydrooctyl-1-trichlorosilane
TEOS — tetraethoxysilane
Ti-pC6 — planar titania ceramic membrane grafted by C6 solution
Ti-pC12 — planar titania ceramic membrane grafted by C12 solution
Ti-tC6 — tubular titania ceramic membrane grafted by C6 solution
Ti-tC12 — tubular titania ceramic membrane grafted by C12 solution
XANES — X-ray absorption near edge spectroscopy
XPS — X-ray photoelectron spectroscopy
YSZ — Yttria-stabilized zirconia
ΔH_v — enthalpy of vaporization
ΔP — pressure difference at the liquid—gas interface
γ_L — surface tension of liquid
θ_{ef} — effective contact angle

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