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Enhancing membrane performance in removal of hazardous VOCs from water by modified fluorinated PVDF porous material

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ABSTRACT

Fluorinated membranes have significant importance in separation due to their inertness, fouling resistance. A novel modification methodology of poly(vinylidene fluoride) (PVDF) membranes was developed employing piranha reagent to activate the fluorinated surface followed by consecutive grafting with 1H,1H,2H,2H-Perfluorooctyltriethoxysilane (FC6). Membranes were implemented in membrane distillation for the removal of hazardous volatile organic compounds (ethyl acetate - EtAc) from water. Octyl group functionalized membranes were also tested for comparison. Membranes were characterized using AFM, ATR-FTIR, SEM, DSC, XRD, goniometric and porometry techniques. Results showed a significant improvement in the membrane performance. Flux of EtAc and PSI changed in the following way between pristine ($J_{EtAc} = 1.8\,kg\,h^{-1}\,m^{-2}$, PSI = $33\,kg\,h^{-1}\,m^{-2}$) and 1-min activated membrane ($J_{EtAc} = 3.0\,kg\,h^{-1}\,m^{-2}$, PSI = $72\,kg\,h^{-1}\,m^{-2}$). Furthermore, for functionalized sample with FC6 the performance was following $J_{EtAc} = 5.2\,kg\,h^{-1}\,m^{-2}$ and PSI = $227\,kg\,h^{-1}\,m^{-2}$. The activation and functionalization influenced significantly material properties. Higher roughness, contact angle and more open structure were noticed after 1-min activation (RMS = 182 nm, CA = 122°, 0.797 µm) in comparison to pristine one (RMS = 142 nm, CA = 116°, 0.551 µm). An improvement of mechanical features was also observed comparing pristine (F_{adh} = 25.2 nN, H = 0.13 GPa, E = 2.10 GPa) and the membrane functionalized by FC6 (F_{adh} = 19.3 nN, H = 0.27 GPa, E = 2.38 GPa).

1. Introduction

Membrane material with controllable water resistance and tunable selectivity, has recently induced a significant interest for separation in particular for water purification processes [1–4]. Innovative separations is required to boost up products quality and production efficiency employing process intensification strategy [5–7]. To improve separation and to expand their application galleries, surface modification and/or functionalization of the membranes should be implemented [3,8–11]. Nature, as an example, show a fascinating design with superior efficiency targeting certain physical properties related to transport across a membrane or encoding vital molecular interactions [12]. Such bionic superhydrophobic morphology, can be fabricated by periodically distributed nano-roughness (heterogeneities) with proper chemical compositions [13]. Subsequently, these materials can be used as antifouling, self-cleaning, anti-icing, anticorrosion, drag reduction, and for adsorption application [14]. Numerous methods have been established to form superhydrophobic surfaces, including chemical etching, chemical vapor deposition, sol-gel technique, template processing, and solution-immersion [12,14,15]. Therefore, to construct a surface with the desired properties, appropriate modification method as well as material should be selected. For separation, poly(vinylidene fluoride) (PVDF) membranes is considered to be exceptionally interesting because of its unique properties and stability. PVDF membranes have attracted researchers and manufacturers for many years because of their chemical and thermal resistance as well as their excellent and high mechanical strength [16–18]. This material frequently used in applications involving industrial secondary effluent treatment,

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Abbreviations: C6, octyltriethoxysilane; FC6, 1H,1H,2H,2H-Perfluorooctyltriethoxysilane; J_{EtAc}, flux of ethyl acetate [$kg\,m^{-2}\,h^{-1}$]; P1-OH, sample activated by Piranha solution during 1 min; P30-OH, sample activated by Piranha solution during 30 min; P1-C6, 1 min activated and functionalized samples by C6 molecules; P30-C6, 30 min activated and functionalized samples by C6 molecules; P1-FC6, 1 min activated and functionalized samples by FC6 molecules; P30-FC6, 30 min activated and functionalized samples by FC6 molecules; PS, Piranha solution; R_a, distance in Hansen space between solvent and solute; RED, Relative Energy Difference; R_o, radius of interaction of the sphere in Hansen space; γ_{cr}, critical surface tension [$mN\,m^{-1}$]; γ_L, liquid surface tension [$mN\,m^{-1}$]; δ_{d1}, δ_{p1}, δ_{h1}, dispersive, polar and hydrogen bonding interactions for first component (water); δ_{d2}, δ_{p2}, δ_{h2}, dispersive, polar and hydrogen bonding interactions for the second component (VOC)

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ultrafiltration processes for water purification [19], membrane contactors operations; *e.g.* volatile organic compounds (VOCs) removal, and membrane distillation (MD) [20,21]. MD is a thermally driven membrane separation process, in which only vapor can pass through the porous hydrophobic membrane whereas liquid is intercepted [22–24]. The hydrophobicity is an elementary requirement for MD process, which can prevent liquid from passing through membrane pores. Although hydrophobic membranes frequently suffer from surface fouling and pore wetting, therefore, surface modification is crucial to optimize performance and overcome challenges [12,14,15]. To design the separation properties of the highly inert PVDF material, chemical activation is required before any modification. Numerous modes of PVDF activation were presented in the literature including treatment with alkaline media, plasma, or ozonolysis [17,25–27]. Nevertheless, these methods have major disadvantages related to efficiency or diminution of mechanical stability i.e. producing high fragile materials. Recently, we developed an efficient method for PVDF membrane activation employing the highly oxidizing piranha solution [28–32]. With a diluted solution of Piranha, it is possible to control the material and physicochemical properties influencing transport and separation across the membrane [28]. The scientific outcomes opened new perspectives for further development of PVDF membranes to achieve advanced separations engaging fine modulation of material properties. In this work, further exploration, tuning and characterization of PVDF materials is presented. Activated PVDF membranes were functionalized by various fluorinated and non-fluorinated moieties with subsequent assessment of their effectiveness in hazardous VOCs removal from water employing a membrane distillation process.

2. Experimental section

2.1. Materials

Polyvinylidene fluoride (PVDF) microfiltration membranes (0.45 µm pore size according to the producer) were purchased from Merck Millipore (USA). Hydrogen peroxide, sulfuric acid, sodium chloride, methanol, glycerol, 1-methyl-2-pirolodine, N,N-dimethylformamide, xylene, toluene, tetrahydrofuran, n-dodecane, cyclohexane, hexane, ethyl acetate were purchase from Avantor Performance Materials (Poland). 1H,1H,2H,2H-Perfluorooctyltriethoxysilane and octyltriethoxysilane were purchased from Abcr chemicals (Germany).

2.2. Instrumentations

The Quantax 200 with XFlash 4010 detector (Bruker AXS machine) was used for scanning electron microscopy (SEM) imaging of membranes. Before measurements, membranes were sputtered with a nanolayer of gold for morphology determination. For EDX measurements, the microscope 1430 VP LEO Electron Microscopy Ltd (England) was used. For atomic force microscopy (AFM), NanoScope MultiMode SPM System and NanoScope IIIa i Quadrex controller, Veeco, Digital Instrument, UK, were applied. PG-X (FibroSystem AB), USA goniometer was applied for material characterization, wettability features. Attenuated total reflection–Fourier transform infrared spectroscopy (ATR-FTIR) were measured using Bruker Vertex 80v ATR-FTIR machine. Solid-state cross-polarization/magic angle spinning nuclear magnetic resonance (CP/MAS NMR) measurements (^{13}C and ^{29}Si) were also performed using Bruker Avance 700 MHz. X-ray diffraction (XRD) analysis were recorded in the 2θ range of 5–60°, at room temperature with 0.02° step and rate of 3°/min using Philips X'Pert PW 3040/60 diffractometer ($K\alpha = 1.5418$ Å) with Cu lamp (30 mA and 40 kV). Rachinger's method with $K\alpha 2/K\alpha 1$ correction was used to determine the full width at half maximum. Pore size was established using Coulter Porometer II (Porometer, Belgium). Gas chromatograph (GC) were performed using Varian 3300 with a TCD detector and PorapakQ packed column (injection port temperature at 200 °C, detector temperature at 220 °C and column temperature at 180 °C).

2.3. Material characterization and methods

The hydrophobic level of the samples was assessed using goniometric measurements. 3 µl drop of ultra-pure liquid measurement after equilibration (5 s) at room temperature was realized determining the apparent contact angle (CA), surface free energy (SFE), and critical surface tension (γ_{cr}). Image J software (Image J, NIH – freeware version) was used for data interpretation with an accuracy of ± 2°. Furthermore, 20–30 individual measurements were conducted and the average values were presented. The following liquids were chosen for CA, SFE and γ_{cr} determination (measurements at 20 °C): water, glycerol, 1-methyl-2-pirolodine, N,N-dimethylformamide, xylene, toluene, tetrahydrofuran, n-dodecane, cyclohexane, hexane. γ_{cr} was calculated based on the Zisman method [33]. SFE Surface free energy values were estimated according to the Owens, Wendt, Rabel, and Kaelble (OWRK) method [34].

The pore size distribution and pore size were established employing the modified bubble point method described in detail elsewhere [35,36]. Initially, sample of the membrane was immersed in a low surface tension wetting liquid (Porefil, $\gamma_L = 16\,\mathrm{mN\,m^{-1}}$), then in a sealed chamber through which dry air flows. The wet-/ dry-run flow method was implemented. All measurements were achieved two to three times for each membrane sample.

Roughness parameters (RMS - root mean squared roughness) were determined using tip scanning mode and scanning sample area of 5 µm × 5 µm. The RMS values for examined membranes were established according to an integrated mathematical algorithm in NanoScope Analysis Software (1.40, Build R3Sr5.96909, 2013 Bruker Corporation). AFM was adopted to samples imaging as well as to tribological characterization (in contact mode). The following parameters describing tribology of the material was assessed: adhesive forces (F_{adh}), Young modulus (E), and nanohardness (H). Details about the tribological analysis of polymeric material were presented elsewhere [28].

2.4. Activation and surface functionalization of PVDF membranes

PVDF membranes were activated by furnishing hydroxyl groups on their surfaces applying 20% piranha solution (**PS**) [28]. The activating agent was prepared by diluting 7.5 ml of concentrated sulfuric acid in 40 ml of deionized water then, 2.5 ml of 30% hydrogen peroxide solution in water was added. Circular **PVDF** membrane with 47 mm diameter and 0.45 µm average pore size were wetted in methanol then directly immersed in 10 ml of activation reagent of piranha solution. Membranes were kept for 1 or 30 min, labeled afterward as **P1-OH** and **P30-OH**, respectively. To quench the reaction after the assigned time, membranes were immersed in a water bath for 5 min and subsequently washed with water and methanol five times each, then dried at 70 °C for 12 h. The resulted membranes were subsequently silanized with 1H,1H,2H,2H-Perfluorooctyltriethoxysilane (**FC6**) and octyltriethoxysilane (**C6**) under argon by immersing **P1-OH** and **P30-OH** in 0.1 M of the analogous grafting solution for 3 h [37] to produce the corresponding functionalized PVDF membranes **P1-C6**, **P1-FC6**, **P30-C6**, and **P30-FC6** respectively.

2.5. Removal of VOCs by air-gap membrane distillation (AGMD)

Ethyl acetate was chosen as VOC to prepare the model aqueous solution (5 wt% of organic phase). AGMD rig is depicted in Fig. 1 whereas the detailed protocol is described elsewhere [38]. Flux of pure water for each membrane sample was determined. Measurements were accomplished at 57 ± 2 °C (feed temperature) and 8 ± 2 °C (permeate temperature) which resulted in the driving force of 160 ± 0.68 mbar as vapor pressure difference. Each experiment was conducted at least 10 h. The chemical composition of the two streams was controlled by GC analysis [37] using Borwin software (JMBS, France) for data processing and acquisition. Analytical parameters: limit of detection (LOD)