Wetting Study of PVDF – Carbon Nanodiscs Membranes for Water Treatment Application via Membrane Distillation

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Abstract. Since 80's, membrane distillation has been identified as a promising water treatment process in various wastewater treatments, such as desalination brine, textile, radioactive and oily wastewater. The demand for membranes with stable flux and prolonged lifespan especially in challenging wastewaters containing oils, surfactants etc. has been increased over the last decade. This research is focused on the preparation and evaluation of poly (vinylidene fluoride) (PVDF) membranes containing functionalized carbon nanodiscs (CNDs). Specifically, carbon nanodiscs, a new family of nanostructured carbon(s), in order to be compatible with the hydrophobic PVDF, were modified with butyltriphenylphosphonium-functionalized hyperbranched polyethyleneimine derivatives of 1300 and 5000 Da molecular weight (PEI-TPP), affording two hybrid nanomaterials, oxCNDs@PEI-TPPs. These hybrids, after their structural characterization using a variety of physicochemical techniques, were coated on the top of the surface of PVDF porous membranes. Their wetting properties against brine wastewater were investigated followed by their evaluation in membrane distillation. Moreover, their fouling behavior in the presence of various natural organic matter such as bovine serum albumin was determined. It was observed that the modified nanocomposite membranes exhibit improved permeability, salt rejection and antifouling properties compare to the neat PVDF membrane.

Keywords: membrane distillation, nanocomposite membranes, carbon discs, hybrid nanomaterials, wetting resistance

1. Introduction

The establishment of membrane –based water treatment technology tends to be as the main technology for the treatment of various wastes in order to recover purified water. Specifically, membrane distillation is a fairly new concept that is steadily gaining popularity in the field of desalination research as it combines the established desalination methods of membrane filtration and heating. [1], [2].

Nowadays, polymeric membranes are considered promising for water treatment applications due to their favorable thermal and chemical resistance, and low cost for large-scale manufacture [3]. Despite these advantages, one major limitation to their utilization lies in surface biofouling which decreases the material's lifespan. Therefore, various strategies have been applied to improve the antifouling or antibacterial properties, including the direct modification of the membrane material, with blending, coating, and grafting modification [4]. The preparation of nanocomposite membranes with the introduction of nanoparticles (NPs) to achieve antibacterial properties has been proven an efficient approach for the control of biofouling [5]. On the top of that, it has been confirmed that hybrid nanomaterials derived by the introduction of functional groups on the structure of carbon-based nanomaterials enhances the antibacterial properties and in parallel reduces the tendency to aggregate due to strong inter-plane interactions [6].

In the present study, macroporous hydrophobic PVDF-HFP membranes coated with oxCNDs@PEI-TPPs hybrid nanomaterials were prepared following a facile method for membrane distillation processes. Characterization was performed using various techniques such as scanning electron microscopy (SEM), liquid entry pressure of water (LEP$_w$) and contact angle. The membranes were tested in direct contact membrane distillation (DCMD) using NaCl solution and their performance was evaluated.

2. Experimental

2.1. Materials

Poly(vinylidene fluoride-co-hexafluoropropylene), PVDF-HFP, (average Mw~455,000, Mn~110,000), and acetone (ACS reagent, >99.5%) were obtained from Sigma-Aldrich (Merck KGaA, Darmstadt, Germany). Hyperbranched polyethyleneimine derivatives (PEI) having molecular weights of 1,300 Da and 5,000 Da (Lupasol® G20, water-free, 98% and Lupasol® G100, water-free, 99%, respectively), were kindly donated by BASF (Ludwigshafen, Germany), while (4-Carboxybutyl)triphenyl phosphonium bromide (TPP), N,N-di(isopropyl) ethylamine (DIPEA) and dialysis tube with molecular weight cut-off 1200 are Sigma-Aldrich products. Carbon discs (CNDs) were purchased from Strem Chemicals, Inc. (France), while N-

hydroxybenzotriazole (HOBt) and 2-(1H-benzotriazole-1-yl)-1,1,3,3-tetramethylura-nium (HBTU) were purchased from Anaspec (San Jose, CA USA).

2.2. Preparation of oxCNDs@PEI(1300)-TPP(C4) & oxCNDs@PEI(5000)-TPP(C4)

The introduction of butyltriphenylphosphonium (butylTPP) moieties to primary amino groups of PEI, with molecular weights of 1300 Da (PEI1300) and 5000 Da (PEI5000), was attained following an analogous method presented in the literature [7, 8]. Specifically, (4-carboxybutyl)triphenylphosphonium bromide dissolved in dry DMF was allowed to react overnight, under argon, with PEI (1:8 molar ratio for PEI1300 and 1:40 for PEI5000), in the presence of equimolar amounts of HBTU, HOBt and DIPEA (4 times of carboxy groups). The crude products were twice precipitated in diethyl ether, while the final products were received after dialysis against deionized water for two days and lyophilization. The successful introduction of the butylTPP groups at the primary amino groups of PEI derivatives was established by FTIR, ^{1}H- and ^{13}C-NMR spectroscopy. Also as determined by ^{1}H and inverse gated ^{13}C NMR spectroscopy, it was found that, on average, 7 and 35 butylTPP groups were conjugated to PEI1300 and PEI5000, respectively.

ATR-FTIR: wavelength (cm^{-1}) = 3345 (v_s, N-H$_2$), 2940 (v_{as}, CH$_2$), 2815 (v_s, CH$_2$), 1640 (Amide I), 1525 (Amide II), 1580 (v, C-C in the aromatic ring), 1453 (δ_s, CH$_2$), 1435 (v, C=C of aromatic groups), 1260 (Amide III), 1100 (v_{as}, C-N), 828 (v, P-F$_6^-$),750 (v, C-H of aromatic groups), 744 (γ CH), 690 (ϕ CC of aromatic groups), 555 and 510 (δ and v, P$^+$-C X-sensitive modes, respectively). ^{1}H-NMR (500 MHz, MeOD-d_4): δ = 1.60 (m, CH$_2$CH$_2$P$^+$Ph$_3$), 1.80 (m, NHCOCH$_2$CH$_2$), 2.05–2.25 (t, NHCOCH$_2$), 2.40–2.80 (m, CH$_2$ of PEI skeleton, CH$_2$NHCO), 3.00 (m, CH$_2$NH$_2$), 3.20 (t, CH$_2$NHCO), 3.40 (m, CH$_2$P$^+$Ph$_3$), 7.55–7.90 (m, aromatic H). ^{13}C-NMR (125.1 MHz, MeOD-d_4): δ = 175.15 (C=O), 134.85 (P$^+$Ph$_3$ para), 133.50 (d, J = 11.5 Hz, P$^+$Ph$_3$ ortho/meta), 130.25 (d, J = 14.57 Hz, P$^+$Ph$_3$ ortho/meta), 124.15 (d, J = 13.56 Hz, P$^+$Ph$_3$ ipso), 53.00–49.30 and 46.40–43.90 (NCH$_2$CH$_2$N), 39.60–36.60 (NH$_2$CH$_2$, CH$_2$NHCO), 35.80 (CONHCH$_2$), 24.5 (d, J = 18.23 Hz, CH$_2$CH$_2$CH$_2$P$^+$Ph$_3$), 22.20 (CH$_2$P$^+$Ph$_3$), 21.50 (d, J = 31.50 Hz, CH$_2$CH$_2$P$^+$Ph$_3$).

Carbon discs were used as raw materials, which were synthesized through the Pyrolytic Kværner Carbon Black & H2 (CB&H) process, while their oxidation was carried out by the widespread Staudenmaier method [9]. In a standard procedure, 300 mg CNDs were added to a mixture of 12 mL H$_2$SO$_4$ and 6 mL HNO$_3$, placed in an ice bath and stirred for 30 minutes. Then, 6 g of potassium chloride powder was added to the above-mentioned mixture in small portions. The reaction was completed after 18 h, and the mixture was deactivated by adding 200 mL of water. Oxidized carbon discs, oxCNDs, were obtained after centrifugation and rinsing

with water until the pH value of the above solution reached 6.5-7, followed by drying. Subsequently, for the preparation of hybrids, 150 mg oxCNDs were dispersed in 50 mL of H$_2$O with the aid of ultrasonication, while the pH was adjusted to 9 with the addition of NaOH solution (6M) and stirred for 24 hours. Then, 300 mg of PEI(1300)-TPP(C4) or PEI(5000)-TPP(C4) dissolved in 50 mL of H$_2$O were added to the oxCNDs dispersion and stirred for 48 hours. The final products oxCNDs@PEI(1300)-TPP(C4) and oxCNDs@PEI(5000)-TPP(C4) were received after centrifugation, washing with water until the pH of supernatant reached the value of 6.5-7.0 and lyophilization [10].

2.3. Nanocomposite PVDF - HFP membranes

A 5% wt. % stock solution of PVDF-HFP in acetone was prepared at 40 ºC. Then, it was added deionized water (5 wt. %) into the solution and left it under stirring for 6 hours. The polymer solution was cast in a 12 cm diameter glass petri dish and left to dry in ambient conditions for 24 hours. After the evaporation of the solvent, porous opaque membrane were obtained via vapor induced phase separation (VIPS) [11]. The hybrid nanomaterials were introduced on the top of the prepared membranes by spin coating of isopropyl alcohol oxCNDs@PEIs dispersions. The samples were span for 180 s at room temperature at a spin speed of 1500 rpm.

2.4. Characterization and performance evaluation

Jeol JSM 7401 F Field Emission Scanning Electron Microscope with Gentle Beam mode was used for morphological characterization of the produced hybrid nanomaterials. To confirm the attachments of TPP groups on the surface of oxCNDs, FTIR spectra were recorded on a Thermo Nicolet 6700 spectrometer equipped with a diamond crystal (Smart OrbitTM, Thermo Electron Corporation) with the attenuated total reflection (ATR) technique. Each sample was scanned 128 times in the range 1000-4000 cm^{-1} and the final spectrum was averaged as a change in % transmittance. The resolution is 4 cm^{-1}.

AKruss DSA-30 drop shape analyzer was used for the contact angle measurements at 25 ºC. Liquid entry pressure (LEP) was calculated based on the Franken equation, which for parameter B=1 becomes equivalent to Young–Laplace's. In this case, takes the following form [12]:

$$LEP = \frac{-2\gamma_L \cos\theta}{r_{max}} \quad (1)$$

The produced membranes were evaluated in DCMD process with effective area of $7 \cdot 10^{-4}$ m^2. As feed solution, 35 g/L aqueous NaCl solution (55 mS/cm) was heated at 80 °C and fed in the module with a flow rate of 200 mL/min, while the permeate side was fed with pure water (8 µS/cm) and flow rate 200

mL/min at a constant temperature of 15°C Bronkhorst CORI-FLOW™ series mass flow meters were recording the mass flows. Each experiment lasted 1 h and the permeate flux and salt rejection were taken as the average value. The permeate flux J (L·m⁻²·h⁻¹) was calculated by the following equation:

$$J = \frac{U_P}{A_m} \quad (2)$$

where, U_P is the volumetric flow rate of vapor permeate, (L/h), A_m is the effective membrane area, (m²).

Salt rejection rate was calculated using the following equation:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (3)$$

Where, R is the percentage of the solute rejection, C_p is the concentration of the solute in the permeate and C_f is the concentration of the solute in the feed.

3. Results & Discussion

The successful development of hybrid materials was verified by FTIR studies. Specifically, in the oxCNDs spectrum (Figure 1), the broad band centered at 3350 cm⁻¹, attributed to the O−H stretching vibrations, as well as the bands at 1710 cm⁻¹, 1413 cm⁻¹ and 1060 cm⁻¹, assigned to the C=O stretching vibrations of the –COOH groups, the O−H bending vibrations and the C–O stretching vibration of alkoxy groups, respectively, verify the presence of hydroxyl and carboxyl groups in the oxCNDs framework. Additionally, the band at 1221 cm⁻¹ is ascribed to C–O stretching of epoxy groups. In both FTIR spectra of PEI-TPPs show the characteristic bands of Amide I, II and III appear at 1640 cm⁻¹, 1525 cm⁻¹ and 1260 cm⁻¹, respectively, which confirmed the presence of the newly formed amide bond in PEI-TPP derivatives. In addition, due to the presence of the butyl-triphenylphosphonium groups, bands at 2940 and 2815 cm⁻¹ attributed to the asymmetric and symmetric stretching vibrations of CH₂ groups, respectively, as well as at 1453 and 744 cm⁻¹ assigned to bending and rocking vibrations of CH₂ groups were observed. The successful interaction of oxCNDs with PEI-TPPs was verified with the appearance of all characteristic bonds of PEI-TPPs as the Amide I and II at 1640 and 1553 cm⁻¹ as well as by the disappearance of the band at 1221 cm⁻¹ which suggested the successful interaction of the primary amino groups of PEI-TPPs with the epoxy groups of oxCNDs.
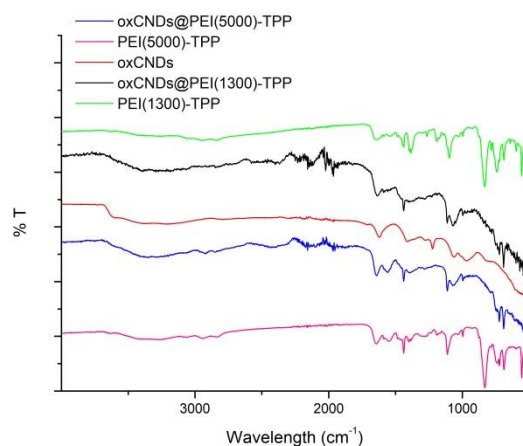

Figure 1. FTIR spectra of oxCNDs oxCNDs@PEI(1300)-TPP(C4) and oxCNDs@PEI(5000)-TPP(C4).

Scanning electron (SEM) microscopy was used to investigate the morphology of oxCNDs after their functionalization with PEI-TPPs. As shown in Figure 2 (A,B,C), the parent oxCNDs, mainly appear as homogeneous disks having round shape with a mean diameter of 1-3 μm. Comparing the SEM images of the parent oxCNDs with those of the functionalized derivatives (Figure 2), it was noticed that the nanodiscs retained their round shape, but appeared with more folds on their surface due to the partial exfoliation of oxCNDs taken place during the functionalization process, which is further evidence of the successful attachment of PEI-TPPs to oxCNDs.
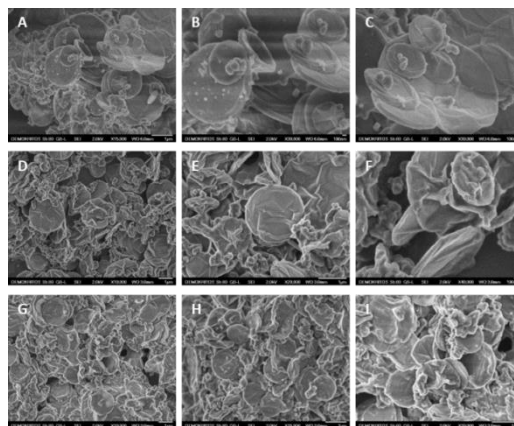

Figure 2. SEM images of oxCNDs (A,B,C), oxCNDs@PEI(1300)-TPP(C4) (D,E,F) and oxCNDs@PEI(5000)-TPP(C4) (G,H,I).

In MD process, wetting resistance is the most significant parameter of any candidate membrane. Two main factors affect this parameter, hydrophobicity and LEP. When the membrane pores are dry, vapor occupies the empty void and separates the feed and distillate streams and prevents the passage of nonvolatile solutes. However, pore wetting does occur and is frequently associated with salt precipitation (scaling) on the membrane surface. As it can been seen in Table 1, the hydrophobicity was estimated by the water contact angle (WCA) of

the pristine membrane is relatively high ($\theta \approx 100°$) and LEP$\approx$2.38 bar, corresponding to a maximum pore radius $\approx$106.5 nm, while, by the introduction of oxCNDs@PEI(1300)-TPP and oxCNDs@PEI(5000)-TPP, the WCA remains almost the same (102° and 105°, respectively), while the LEP slightly increases to 2.5 and 2.88 bar, respectively. This means that the hybrid nanomaterials enhance the wetting resistance and this ability is expected to affect the properties of the membranes in membrane distillation. Indeed, the results from the experiments of DCMD conclude in the increase of permeate flux, from 5.1 to 6.9 and 9.7 LMH, for oxCNDs@PEI(1300)-TPP and the oxCNDs@ PEI(5000)-TPP, respectively. Also, the salt rejection for the both cases becomes from 99.97 to 99.99%.

Table 1. Results of membrane characterization & evaluation

Membrane	WCA (°)	LEP (bar)	R_{max} (nm)	Permeate Flux (LMH)	Salt Rejection (%)
PVDF-HFP	100	2.38	106.5	5.1	99.97
oxCNDs@ PEI (1300)-TPP	102	2.5	121.4	6.9	99.99
oxCNDs@ PEI (5000)-TPP	105	2.88	131.4	9.7	99.99

4. Conclusions

In summary, oxCNDs@PEI-TPPs were successfully prepared and applied as a coating in PVDF-HFP membranes. The characterization was conducted by various methods, while their performance in DCMD was evaluated. The experimental results showed that the application of hybrid nanomaterials had significant effects on the overall properties of the membrane. Specifically, DCMD experiments showed that the nanocomposite membrane had improved permeability, while retaining excellent salt rejection. A further investigation of the properties of the nanocomposite membranes need to be explored for their best utilization in water treatment technology.

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