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Surface hydrophilicity modification of PVDF membranes with an external electric field in the phase inversion process

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Abstract. To increase the surface hydrophilicity of PVDF membranes, in this paper, an electric enhancing method was adopted to treat PVDF nascent membranes during the phase inversion process. It was found that when PEG 600 was taken as the additive, the surface water contact angle of the PVDF membrane treated under 2 kV electric field was decreased from 84.0° to 65.7°. The reason for the surface elements change of the PVDF membranes prepared under the electric field was analyzed in detail with the dielectric parameters of the polymer dope solutions. Results from BSA adsorption experiment showed that the antifouling ability of the external electric field-treated membranes was distinctly enhanced when compared with that of the untreated membranes. The amount of BSA adsorbed by the treated membranes was lower by 38-43%. Compared with the common chemical reaction methods to synthesize hydrophilic additives or membrane materials, the electric field-assisted processing method did not involve any additional chemical synthesis process and it was capable of realizing better hydrophilicity.

Keywords: PVDF; ultrafiltration; anti-fouling

1. Introduction

Ultrafiltration (UF) membrane is widely used in the membrane industry (Baker 2012). UF membranes can be classified into hollow fiber membranes and flat sheet membranes. The former have high packing density and large membrane surface-to-volume ratio, and are deemed to be more economical than flat sheet membranes, whereas the latter possess higher mass transfer coefficient, are easier to clean, and have better antifouling property. Furthermore, flat sheet membranes with a support layer present stronger mechanical strength, are easy to operate, and are easy to maintain; all features that are important from an industrial standpoint (Baker 2012). In the wastewater treatment field, using UF membrane bioreactors (MBR) method is a rapidly developing technology (Robles *et al.* 2013). However, membrane fouling caused by biological macromolecules in polluted water limits the further potential wide application of MBR. Hence, a process for improving the antifouling performance of UF membranes is particularly urgent for enabling its wide-spread use. In general, a strongly hydrophilic membrane possesses strong antifouling ability. The common used methods for increasing the surface hydrophilicity of the

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membranes include surface coating or grafting and blending method (Zhang *et al.* 2014, Jamshidi Gohari *et al.* 2014, Liu *et al.* 2013). In one of our previous works, we employed an electric enhancing technique to improve the antifouling performance of polyethersulfone UF membrane (Wang *et al.* 2010). In that process, an electric field is applied to the nascent PES membranes before phase inversion by immersion precipitation.

It is widely known that poly vinylidene fluoride (PVDF) is also a kind of membrane material with many good performances. However, the hydrophilicity of PVDF is not strong and the water contact angle on the surface of pure PVDF homogeneous flat film is about 82° (Mark 1999). Therefore, surface hydrophilicity modification is often performed for PVDF membranes to decrease the water contact angle. In addition, PVDF is also a piezoelectric electroactive polymer (EAP). It can store charges and becomes electret under certain conditions. The space charge distribution of a PVDF film can be improved by some methods such as blending with polar materials, surface modification and applying D.C. electric field (Lei *et al.* 2009, An *et al.* 2011).

To enhance the surface hydrophilicity of PVDF membranes, in this study, we still adopt the previous reported electric enhancing method to treat PVDF membranes during the phase inversion process. Our motivation is that since PVDF is a piezoelectric electroactive polymer, its surface hydrophilicity will be more easily changed when applying the electric enhancing technique. As reported in this work, we indeed find that the surface contact angle of PVDF membranes can be easily decreased for about 20° when using this method. Compared with our previous work, another novelty of this work is that the mechanism of elements change at the surface of the PVDF membranes prepared under the electric field is also researched in detail with the dielectric parameters of the polymer dope solutions. In addition, the effects of the external electric field on the membrane potential, antifouling property, tensile strength, and separation performance of the PVDF UF membranes are also measured.

2. Experiment

2.1 Materials

PVDF (Solef 6010) was purchased from Solvay, Belgium. *N*-methyl-2-pyrrolidone (NMP, AR) and poly (ethylene glycol) (PEG; molecular weight = 600, 800, 1000, and 1500 g·mol⁻¹) were used as pore formers which were purchased from Tianjin Kermel Chemical Reagents Development Centre, China. Bovine serum albumin (BSA, molecular weight = 68,000 g·mol⁻¹) was purchased from BeiJing AoBoXing Bio-tech Co., Ltd., China.

2.2 Membrane preparation

The schematic diagram of the experimental setup is shown in Fig. 1. Two stainless steel plates $(22.5 \times 17.5 \text{ cm})$ were used as electrodes. The positive electrode was fixed on the top of the box (top electrode) while the negative electrode (bottom electrode) was supported by a polyamide stand. The gap between the top electrode and the bottom electrode was 2.0 cm. The voltage of the top electrode was regulated with a D.C. power, which was set at 2 kV. A stable direct current static electric field formed after the D.C. powder was turned on for about 20 minutes.

The membranes were prepared by classical immersion precipitation phase inversion method at room temperature (about 20°C) with a relative humidity of about 75 %. PVDF powders were dried at 60°C for at least 24 h before use. Dope solutions were prepared by blending PVDF, PEG, and



Fig. 1 Schematic diagram of experimental setup for preparation of membranes

NMP. Concentrations of PVDF and PEG in the casting dope solutions were 16 wt.% and 3 wt.%, respectively. After completely dissolving the components and degassing, the homogeneous casting solution was poured onto a glass plate. The solution was spread by means of a hand-casting knife (the height of the casting knife was adjusted to give a 350μ m thick layer) while moving the glass plate rapidly for 30 seconds on the bottom electrode. After 30 seconds, the glass plate was immersed immediately into a coagulation water bath at 17° C. After being peeling off from the glass plate, the membranes were rinsed with distilled water and stored in distilled water for at least 24 h before further use.

2.3 Measurement of dielectric constant of the polymer dope solutions

To understand the electrical response of the polymer dope solutions under the influence of electric field, the dielectric constants of PVDF/NMP (19/81), PEG 600/NMP (19/81), PVDF/PEG 600/NMP (9.5/9.5/81), and PVDF/PEG 600/NMP (16/3/81) solutions were measured at room temperature by a dielectric constant measurement instrument (PCM-1A, Nanda Wanhe Science and Technology Co., Ltd, Nanjing, China).

2.4 Characterization of morphology and surface groups and elements of the membranes

Morphologies of the top surface and cross-section of the membranes were observed with a scanning electron microscope (SEM, FEI Sirion, Holland). Samples were prepared by fracturing the membranes cryogenically in liquid nitrogen. Each sample was coated with a thin layer of gold by sputtering before being viewed with the SEM.

Surface groups of the membranes were analyzed by attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), which was performed on a Nicolet FT-IR 360 spectrometer, where the angle of incidence was 45° with ZnSe crystal that was in contact with the surface of the membrane. Transmittance spectra were obtained in 4000-500 cm⁻¹ region with a resolution of 4 cm⁻¹. To obtain a clear transmission spectrum for each sample, 64 scans were averaged.

The molar contents of F, C and O on the surface of the membranes were also analyzed by an X-ray photoelectron spectrometer (K-Alpha X-ray Photoelectron Spectrometer system, Thermo Fisher Scientific Inc., USA).

2.5 Measurement of water contact angle

Surface hydrophilicity of the membranes was determined by measuring the water contact angle using a CA instrument. Droplets of deionized water spreading on the dried membranes (20×20 mm) were used for measurement of this parameter. To minimize the experimental error, measurements from five randomly chosen locations in each membrane were averaged.

2.6 Measurement of porosity

Membrane porosity was calculated after measuring the dry and wet mass of the membranes. First, the membranes were placed in an air-circulating oven at 60°C for 24 h for measuring the dry mass. Then the dried membranes were immersed in *n*-butanol for 24 h at 20°C to obtain the wet mass. The membrane porosity (ε_p) was calculated using the following equation

$$\varepsilon_{\rm p} = \frac{\left(m_w - m_d\right)/\rho_w}{\left(m_w - m_d\right)/\rho_w + m_d/\rho_p} \times 100\% \tag{1}$$

where m_w and m_d are the mass of wet and dry membranes, respectively. ρ_w and ρ_p are the densities of *n*-butanol (0.81 g/cm³) and PVDF (1.78 g/cm³), respectively. For each kind of membranes, five samples were measured to obtain the average result and the stand deviation.

2.7 Measurement of tensile strength

Tensile strengths of the membranes were measured on an in-house assembled film mechanical test instrument. Samples were prepared by cutting the wet membranes $(15 \times 50 \text{ mm})$. The tensile rate was 3 mm/min. The maximum break tensile force was recorded and was used to calculate the tensile strength. Over ten replicate measurements of tensile strength were performed at room temperature and the average value was calculated with a standard deviation (SD) being less than 5%.

2.8 Measurement of ultrafiltration performance

Ultrafiltration experiment was carried out using an in-house dead-end filtration equipment. The effective membrane surface area was 6.60 cm². All ultrafiltration experiments were conducted at 25°C and the feed pressure was 0.1 MPa. The measurement of flux and concentration of the permeation was performed as described here. For the first 30 min, the membranes were compacted at 0.15 MPa to get a steady flux. Subsequently, the flux of pure water was measured under 0.1 MPa. After measuring the flux of pure water, the solution was changed to aqueous BSA solution (0.1 g·L⁻¹). At least 5 measurements of the flux were collected to obtain an average value. The concentration of BSA in both the feed and the permeate solutions were measured by UV-VIS spectrophotometer (T6, Beijing Purkinje General Instrument, China) at 280 nm. The permeation flux, $J (L \cdot m^{-2}h^{-1})$ was defined as

$$J = \frac{V}{A\Delta t} \tag{2}$$

where V was the permeation volume, A was the effective membrane surface area, and Δt was the permeation time. Rejection (R) was defined with the following equation

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

where C_p and C_f (mg·mL⁻¹) were the concentrations of BSA in the permeation and feed sides, respectively.

2.9 Measurement of protein adsorption

To evaluate the fouling resistance of untreated and treated membranes, the following protocol was used for evaluating BSA adsorption. Membrane (surface area 18 cm²) was soaked thoroughly in 0.1 M phosphate buffer solution (PBS; pH 7.4) for 30 min. Both the treated and the untreated membranes were put in flasks containing freshly prepared solution of BSA (1.0 mg·mL⁻¹) in PBS (20 mL). These flasks were then incubated in a water bath at 25°C for 24 h. The concentration of BSA in the solution before and after adsorption was measured and the amount of adsorbed protein calculated. At least three measurements were performed for each sample.

2.10 Measurement of membrane potential

Membrane potential was measured in KCl solution at room temperature (pH = 7.0). The membranes (10.4 cm²) were pinched with silicone rubber rings between two polyamide half-cells (95 cm³ each). Concentrations of KCl used in these experiments were 1×10^{-3} , 2×10^{-3} , 3×10^{-3} , 4×10^{-3} , 5×10^{-3} , 6×10^{-3} , and $7 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$. Each compartment was filled with KCl solution (88 mL) and peristaltic pump was used to circulate the solution (65 mL·min⁻¹). Through the experiment, the bottom surface of the membranes was in contact with $1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ KCl solution, while the top surface of the membrane was in contact with KCl solution of higher concentrations. The electrical potential difference of the cell (E_{cell}) was measured with two Ag/AgCl electrodes, which were inserted directly into the two compartments. The membrane potential, E_m (mV) was defined as follows

$$E_m = E_{cell} - \frac{RT}{F} \ln \frac{c_2}{c_1}$$
(4)

where *R* was the ideal gas constant, *T* was the absolute temperature, *F* was the Faraday constant, and c_2 and c_1 were the concentrations of Cl⁻ ions ($c_1 > c_2$) in bulk solutions below and above the membrane, respectively.

3. Results and discussion

3.1 Effect of external voltage on morphology and surface groups and elements

The cross-section (Fig. 2) and top surface (Fig. 3) morphologies of two PVDF membranes, prepared at external voltages of 0 and 2 kV, show that the membranes have asymmetric structure consisting of a dense top skin layer and a porous support layer. No obvious difference between the membranes prepared under the two different conditions (external influence of 0 and 2 kV; same PEG molecule) is observed in the SEM images.



Fig. 2 Cross section morphology of membranes with PEG 1500 as additive



Fig. 3 Top surface morphology of membranes with PEG 1500 as additive

ATR-FTIR spectra of the membranes prepared with PEG 1500 as the porogen under the two different conditions show that there are no significant differences in the major transmittance peaks (Fig. 4). Consequently, the functional groups in the surface of the two membranes are similar, indicating that the external voltage has no influence on the chemical groups on the membrane surface.



Fig. 4 ATR-FTIR spectra of top surface of membranes with PEG 1500 as additive

Table 1 lists the molar contents of F, C, and O on the surface of six PVDF membranes. For any two membranes prepared with the same dope solution, the F content on the surface of the membrane processed under the electric field is higher than that of the membrane prepared without the electric field. The reason underlying the increased fluorine content on the surface of the membranes prepared under the electric field of 2 kV can be attributed to the following two aspects: (1) in itself, F exhibits larger response under the influence of electric field (Lei et al. 2009, An et al. 2011). Consequently, it might have accumulated on the surface of the membranes upon the application of D.C. electric field; and (2) when PEG was used as an additive in the polymer dope solution, the strong movement of the PEG groups would favor further accumulation of fluorine on the surface of the membranes. This speculation was further confirmed from the results of the dielectric constant of the polymer dope solutions, as listed in Tables 2 and 3.

Membrane	F	С	-
PVDF (0kV)	35.5	64.5	

Table 1 Molar content (%) of F, C, and O on the surface of the membrane

Membrane	F	C	0
PVDF (0kV)	35.5	64.5	_
PVDF (2kV)	36.8	63.2	_
PVDF/PEG 600 (0kV)	38.2	57.3	4.5
PVDF/PEG 600 (2kV)	40.5	54.7	4.8
PVDF/PEG 1500 (0kV)	42.3	51.3	6.4
PVDF/PEG 1500 (2kV)	44.6	48.4	7.0

Table 2 Dielectric constant of the raw materials

Name	3	Structure	Reference
PVDF	7.82		(Zak <i>et al.</i> 2011)
PEG 600	11.60	H [0] n - H	(Naokazu and Tetsuya 1964)
NMP	32.17		(Naokazu and Tetsuya 1964)

Table 3 Experimental dielectric constant of the dope solutions

Number	Mass ratio of the solution	3
(1)	NMP	32.2
(2)	PVDF/NMP = 19/81	19.0
(3)	PEG 600/NMP = 19/81	23.4
(4)	PVDF/PEG 600/NMP = 9.5/9.5/81	23.3
(5)	PVDF/PEG 600/NMP = 16/3/81	24.6

According to the composition of the solutions (2) and (3), as listed in Table 3, the independent addition of PVDF and PEG to NMP resulted in similar response status under the electric field, given the fact that their contributions to the dielectric constant of the solutions are similar. However, when PVDF and PEG are added together to NMP (as in the case of solution (4)), the effect of PVDF was totally obscured by PEG, given the fact that the dielectric constants of solutions (3) and (4) are the same. This implies that the response rate and the movement of PEG groups are rather faster than that of the PVDF groups.

The movement of the PEG groups is not independent. Instead, it would also cause the PVDF groups to move along, as can be explained from the observed difference in dielectric constant between the solutions (4) and (5). The viscosity of the solution (5) is larger than that of the solution (4) due to the larger amount of PVDF added to the solution. In general, for any liquid or solution, a decrease in viscosity (such as induced by the increased temperature) results in the decrease of its dielectric constant because of the faster movement of the molecules or groups. Therefore, the movement of the PEG groups must be confined upon the addition of more PVDF, which induced the increase in dielectric constant from 23.3 to 24.6. This also implies that the movement of PEG groups can cause the movement of PVDF groups, inducing more fluorine elements to accumulate on the surface of the membranes.

3.2 Effect of external voltage on surface hydrophilicity

Change of water contact angle of the membranes with the external voltage is shown in Fig. 5. When no PEG is added, the water contact angle of the 0 kV and 2 kV membranes is similar, and the contact angle values of the neat PVDF membranes are larger than that of the membranes treated with the external electric field. In addition, when PEG is added as a pore former, the water contact angle of all 2 kV membranes decreases when compared to that of 0 kV membranes. This result indicates that the external voltage induces higher hydrophilicity to the membranes.

Table 4 lists the water contact angle values measured on the surface of PVDF membranes, as reported in similar previous studies. As is seen, the reported water CA values measured on the surface of PVDF/PEG-400 and pure PVDF membranes, and that on the surface of the PVDF/PEG



Fig. 5 Effect of the external voltage on water contact angle of membranes

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Table 4 Water contact angle of PVDF membranes

Polymer dope composition	CA (°)	Reference
PVDF/PEG-400/NMP = 17/5/78	84.9	(Mansourizadeh and Ismail 2012)
PVDF/NMP = 12/88	85.0	(Pezeshk et al. 2012)
PVDF/L2MM(PEG-200)/NMP = 12/3/85	77.0	(Pezeshk et al. 2012)
PVDF/L2MM(PEG-600)/NMP = 18/3/79	80.7	(Pezeshk et al. 2012)
PVDF/L2MM(PEG-200)/NMP = 18/3/79	77.3	(Pezeshk et al. 2012)
PVDF/PEG 600/NMP = 16/3/81 (0 kV)	84.0	Present work
PVDF/PEG 600/NMP = 16/3/81 (2 kV)	65.7	Present work

600 membrane prepared in this work, have almost the same value of approximately 84° to 85° . Pezeshk (Pezeshk *et al.* 2012) synthesized a new type of hydrophilic macromolecule (known as L2MM) using MDI (4,4'-methylenebis (phenyl isocyanate)) and PEG-600 or PEG-200, which when added to the polymer dope solution changes the hydrophilicity of the resulting PVDF membrane. As listed in Table 4, the CA value measured on the surface of the PVDF membrane prepared with L2MM additive is approximately 77° , decreasing only by approximately 8° . However, the CA value measured on the surface of the PVDF membrane prepared under the electric field of 2 kV has reached as low as 65.7° . Given the advantages that the electric field-assisted processing method does not involve any additional chemical synthesis process to prepare new additive, and that it is capable of realizing better hydrophilicity, the method can be regarded an "environment-friendly technology" as against the conventional synthesis methods.

3.3 Effect of PEG molecular weight on porosity

The porosity of each type of membrane is listed in Table 5. The results reveal that the membrane porosity increases with increase in the molecular weight of PEG, as a result, leading to an increase in the permeation flux of the membranes. The average tensile strengths of the membranes prepared under 0 and 2 kV external voltage in the presence of PEG 1500 were 0.82 MPa and 0.76 MPa, respectively. The lower tensile strength of the membranes prepared under 2 kV also indicated that the porosities in them were larger than those in the membranes prepared at 0 kV.

These results are in agreement with the result of UF obtained in this study (Fig. 6). With an increase in the molecular weight of PEG additive, an upward trend in the value of $J \times R/100$ is observed for series of membranes prepared in the presence or absence of external voltage. Highest

Type of membrane	0 kV	2 kV
PVDF	58.6 ± 0.8	58.9 ± 0.6
PVDF/PEG 600	62.7 ± 2.5	64.4 ± 3.2
PVDF/PEG 800	65.4 ± 2.1	68.1 ± 4.3
PVDF/PEG 1000	68.5 ± 3.3	70.2 ± 3.9
PVDF/PEG 1500	72.1 ± 2.8	76.4 ± 3.7

Table 5 Porosity ε_n (%) of PVDF membranes



Fig. 6 Permeation properties of membranes with different PEG additives

values of $J \times R/100$ in this study, i.e., 34.06 (0 kV) and 39.22 (2 kV), are observed when PEG 1500 is used as the additive.

On the one hand, because of the entanglement of molecular chains, the mobility of PEG reduces with increase in its molecular weight. Thus, a larger portion of the high-molecular weight PEG is likely to be trapped inside the dope during phase inversion. On the other hand, PEG shows good solubility in water, which is used in the coagulation bath. Consequently, PEG can dissolve in water and leach out during the solidifying stage, leaving macrovoids inside the membranes.

3.4 Effect of external voltage on BSA adsorption

Effect of PEG molecular weight and external voltage on the adsorption of protein on the membrane surface is shown in Fig. 7. It is obvious that the amount of protein adsorbed on the membrane surface increases linearly with increasing molecular weight of PEG. However, with the same PEG additive, the external voltage-treated membranes exhibit lower protein adsorption capacity than the untreated membranes. The amount of protein adsorbed by the external voltage-treated membranes is reduced by 38-43% when compared with that by the untreated membranes. In particular, the membrane with PEG 600 additive, the adsorption amount (132.5 μ g·cm⁻²) is reduced by 43%. Therefore, the antifouling ability of the external electric field-treated membranes was distinctly enhanced when compared with that of the untreated membranes.

However, the mechanism of BSA adsorption on the surface of the membranes is complicated because it involves an unsolved problem between the common used nomenclature 'hydrophilicity' and two different basic attraction forces: van der Waals attraction force and Coulomb force (van Oss 2006). The van der Waals force includes dispersion force, dipole/dipole force and dipole/induced dipole force. For any molecules, the dispersion attraction force always exists. For the neutral but polar molecules, (e.g., water and ethanol), the dipole attraction forces also exist. However, when the molecules are not electric neutral molecules (some charges existing in the molecules), the Coulomb electric attraction force will exist between two charged molecules. The key problem is the common adopted 'hydrophlicity' parameter (using water as a probe to test the molecular force of a solid surface) does not include the Coulomb force. For most adsorption systems composed of neutral solid material, the common concept that 'when hydrophilicity

increases, the anti-fouling ability will also increase' maybe is right. However, for an adsorption system composed of a charged solid material and a charged molecule, there is no reliable evidence about increasing the hydrophilicity of a solid surface must induce a decreasing in the adsorption amount.

In aqueous solution, because BSA molecules show negative potential (the isoelectric point of BSA appears at pH 4.8), a Coulomb force will exist between BSA molecules and the charged PVDF membranes, which is a negative-negative repulsion force. Although the hydrophilicity of the charged PVDF membranes increases with the increase of molecular weight of PEG (Fig. 5), the negative-negative repulsion interaction becomes weak with the molecular weight of PEG because the membrane potential increases (Fig. 8). Therefore, the total BSA adsorption amount could also increase because the Coulomb force between BSA and the membranes seems to be an important interaction as discussed in the next section.



Fig. 7 Amount of BSA adsorbed on the membrane surface



Fig. 8 Membrane potential of the membranes



Fig. 9 Effect of membrane potential on the amount of BSA adsorbed; (a) 0 kV PVDF membrane; and (b) 2 kV PVDF membrane

3.5 Effect of external voltage on membrane potential

Regardless of the method of preparation, the membrane potential increases with increase in the molecular weight of PEG (Fig. 8). When membranes prepared with the same PEG are considered, the membrane potential of 2 kV membrane is lower than that of the 0 kV membrane. Furthermore, the membrane potentials of all 2 kV membranes are negative (Fig. 8), which indicates that negative charges exist at the top surface of the 2 kV membranes. Because a positive electric field is formed during the preparation of the membranes, negative charges will be held permanently at the top surface of the prepared membranes. The possible reason for the charge accumulation should be the asymmetrical distribution of surface F, C and O elements all changed when external electric-field was applied, and the detailed reasons of the changes have been discussed in Section 3.1.

Fig. 9 shows the effect of membrane potential on the protein adsorption. The amount of BSA adsorbed increases with an increase in the membrane potential. The isoelectric point (IEP) of BSA is at pH 4.8, and BSA molecules show negative potential when the pH value is higher than 4.8. Therefore, in this study, the amount of BSA adsorbed increases with an increase in the membrane potential because a negative-negative electrostatic repulsive force exists between the surface of the membranes and BSA molecules. This suggests that the adsorption of BSA on the membranes depend mainly on the membrane potential.

4. Conclusions

To increase the surface hydrophilicity of PVDF membranes, the electric enhancing method was adopted to treat PVDF nascent membranes during the phase inversion process. When PEG 600 was taken as additive, the surface water contact angle of the PVDF membrane treated under 2 kV electric field was decreased from 84.0° to 65.7°. The reason for the surface elements change of the PVDF membranes prepared under the electric field was also analyzed in detail with the dielectric

parameters of the polymer dope solutions.

Results from BSA adsorption experiment showed that the antifouling ability of the external electric field-treated membranes was distinctly enhanced when compared with that of the untreated membranes. The amount of BSA adsorbed by the treated membranes was lower by 38-43%. Compared with the common chemical reaction methods to synthesize hydrophilic additives or membrane materials, the electric field-assisted processing method did not involve any additional chemical synthesis process and it was capable of realizing better hydrophilicity.

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