Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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Yanping Wang[a]; Xin Zhang[a]; Baoli Shi[a]; Lina Jia[a]; Xiaoguang Zhou[a]
[a] Polymer Membrane Laboratory, College of Science, Northeast Forestry University, Harbin, China

To cite this Article Wang, Yanping , Zhang, Xin , Shi, Baoli , Jia, Lina and Zhou, Xiaoguang(2010) 'Preparation of Anti-Fouling Polyethersulfone Ultrafiltration Membrane by an External High Voltage Electric Enhancing Method', Separation Science and Technology, 45: 16, 2280 — 2286

To link to this Article: DOI: 10.1080/01496395.2010.488259

URL: http://dx.doi.org/10.1080/01496395.2010.488259

Separation Science and Technology, 45: 2280–2286, 2010
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ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496395.2010.488259

Preparation of Anti-Fouling Polyethersulfone Ultrafiltration Membrane by an External High Voltage Electric Enhancing Method

Yanping Wang, Xin Zhang, Baoli Shi, Lina Jia, and Xiaoguang Zhou
Polymer Membrane Laboratory, College of Science, Northeast Forestry University, Harbin, China

In this article, a novel method of applying high voltage (1–5 kV) to the conventional immersion precipitation phase inversion process was used to prepare polyethersulfone ultrafiltration membranes when PVP (30 K) was used as an additive. The effects of the external electric field on the structure, surface functional groups, membrane potential, and surface hydrophilicity of the membranes were researched. Bovine serum albumin (BSA) adsorption amounts on the membranes and the separation performances of the membranes were measured. It was found that the external electric field influenced the surface carbonyl groups, surface hydrophilicity, and potential of the membranes. With the increase of the external voltage, the surface hydrophilicity and the membrane potential decreased. It seemed that the external voltage had no influence on the cross-section structure of the membranes, but the surface porosity density slightly reduced when the external voltage increased. In basic BSA solution, the protein adsorption amount on the electric enhanced membranes was distinctly reduced when compared with an un-enhanced membrane, and the rejection was also improved. Consequently, the prepared electric enhanced PES membranes had distinctive anti-fouling properties.

Keywords electric field; membrane potential; polyethersulfone; ultrafiltration membrane

INTRODUCTION

Ultrafiltration (UF) polymer membranes are widely used to separate micro-solutes from water solutions in pharmaceutical, biotechnology, medical, food, beverages, potable water, dairy, metallurgical, and electro-coating industries (1–3). However, membrane fouling from protein adsorption will result in a sharp decline in permeation flux and the increase of recovery cost. The surface property of the polymer membranes and membrane materials is one of the key factors for the protein adsorption on the membrane surface. There were lots of reports on preparing anti-fouling membranes in recent years. A recent review article written by Van der Bruggen gave a detailed introduction on the various methods of increasing anti-fouling properties (4). According to this paper, two distinct categories of methods are usually adopted to decrease the protein adsorption. One category is modifying the bulk polymers or the surface of polymer membranes through chemical reaction methods. Another category is the blending method, which is a simple and cheap physical method. Compared with the chemical method, the shortcoming of blending is that the applications are limited by the miscibility of some hydrophobic and hydrophilic polymers.

Immersion precipitation phase inversion is an important technique for the preparation of polymeric asymmetric UF membranes. For this technique, some additives are usually added in polymer casting solution, such as polyvinylpyrrolidone (PVP) or polyethylene glycol (PEG), to enhance the performance of UF membranes. The commercial UF and MF membranes made from polysulfone (PSf) and polyethersulfone (PES) are mostly produced by using PVP as an additive (1,2).

In recent years, high voltage devices have been widely applied to fabricate many polymeric nanoscale fibers (e.g., PES nanofibers) by the electrospinning technique. Non-woven mats made from these nanofibers can be used as filtering media to treat wastewater (5,6). In order to further enhance the performances of UF membrane prepared by the conventional phase inversion technique, an externally applied electric enhancing technique was used to prepare PES UF membranes (using PVP 30 K as additive) in this experiment. The distinctive feature of this method was that high voltage (1–5 kV), generated from a common D.C. power used in the electrospinning technique, was applied to the membranes during the whole immersion precipitation phase inversion process. The aim was to permanently change the final surface properties of the PES membranes. To our knowledge, we believe that this method is a new method for the application of high voltage devices to the polymeric membrane fabricating techniques.

In this work, the effects of the external electric field on the structure, surface functional groups, membrane

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Received 20 January 2010; accepted 21 April 2010.

Address correspondence to Baoli Shi, College of Science, Northeast Forestry University, Harbin, 150040, China. Tel.: +86 451 8219 2327. E-mail: shi_baoli@yahoo.com

potential, and surface hydrophilicity of the membranes were researched. In addition, the protein (BSA, bovine serum albumin) adsorption amount on the PES membranes and the separation performances of the membranes were also measured in this experiment.

EXPERIMENTAL

Materials

PES (Ultrason E 6020P) was purchased from BASF Co., Germany. PVP (30 K) was purchased from Fluka Chemika, Switzerland. Bovine serum albumin (BSA) (M_w was 68,000 Da) was purchased from Beijing AoBoXing Bio-tech Co., Ltd., China. *N*-methyl-2-pyrrolidone (NMP, analytical grade) was purchased from Tianjin Kermel Chemical Reagents Development Centre, China. They were directly used without purification. Distilled water was used throughout this study.

Preparation of PES Membranes by External Electric Enhancing Method

A D.C. electric field was formed with a self-made equipment. The schematic diagram of the experimental setup is shown in Fig. 1. Two stainless steel plates (22.5 cm in length, 17.5 cm in width) were used as electrodes. The top electrode (positive electrode) was fixed. The position of the bottom electrode (negative electrode) was controlled with a crank setup. When the bottom electrode was moved upwards, the smallest gap between the top electrode and the bottom electrode was 2.0 cm. When it was moved downward, it would dip into the coagulation water bath. The voltages of the top electrode were 0, 1, 2, 3, 4, and 5 kV, which were regulated with a D.C. power.

PES membranes were prepared by the conventional immersion precipitation phase inversion method. PES powder was dried at 100°C for at least 24 h before use. Homogeneous casting solution was prepared by dissolving PES and PVP in NMP at 50°C. The concentration of PES and PVP in the casting solution was 17wt% and 4wt%, respectively. After degassing, the casting solution was cast on a glass plate at room temperature (18°C), and then the glass plate was rapidly moved onto the bottom electrode. This process needed about 10 seconds. Then, the bottom electrode was lifted and the positive electrode was switched on simultaneously. After 40 seconds, the bottom electrode was declined into the coagulation water bath (17°C). Finally, the membranes were kept in distilled water for at least 48 h until all of solvent was removed.

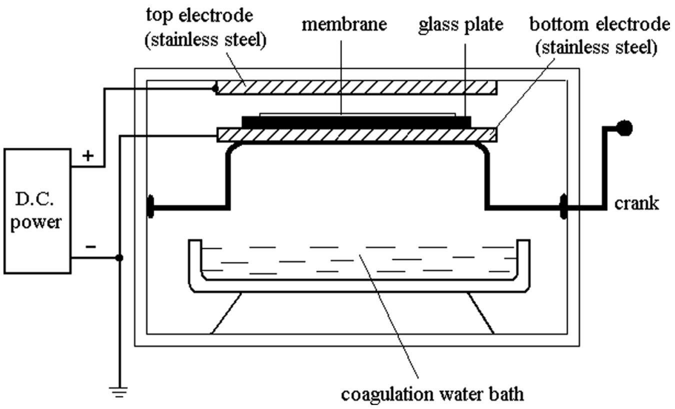


FIG. 1. Schematic diagram of experimental setup for preparation of PES membranes by external electric enhancing method.

Characterization of Membrane Morphology by SEM and AFM

The cross-section and surface morphologies of the prepared PES membranes were examined by a scanning electron microscope (FEI Quanta 200, USA) and an atomic force microscope (Pico Plus, Molecular Imaging Corporation). For the SEM measurement, the samples were frozen in liquid nitrogen and fractured. After sputtering with gold, the cross-section of the membranes was viewed with the SEM.

Characterization of Surface Functional Groups of PES Membranes by ATR-FTIR Spectroscopy

The functional groups at the surface of the PES membranes were analyzed by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) technique, which was performed on a Nicolet FT-IR 360 Spectrometer. The surface of the membranes was in contact with a ZnSe crystal with a 45° angle of incidence. Absorbance spectra were obtained in the region of 4000–600 cm^{-1} with a resolution of 4 cm^{-1}. 64 scans were averaged in order to obtain clear absorption spectra of each sample.

Measurement of Membrane Potential

The membrane potential of the PES membranes was measured in KCl solutions at four pH values (2.2, 4.8, 7.0, and 8.0) through a method as described in Ref (7). The membranes (area of 10.4 cm^2) were clamped between two self-made polyamide half-cells with the volume of 95 cm^3 by using silicone rubber rings. KCl solutions with the concentrations of 1×10^{-3} mol/L, 2×10^{-3} mol/L, 3×10^{-3} mol/L, and 4×10^{-3} mol/L were used. Each compartment was filled with 88 mL of KCl solution, which was circulated through its compartment by a peristaltic pump at a rate of 80 mL/min. The bottom surface of the membranes was contacted with the solution of 1×10^{-3} mol/L. The top surface of the membranes was contacted with other KCl solutions.

The electrical potential difference of the cell (E_{cell}) was measured with two Ag/AgCl electrodes which were inserted directly into the bulk solutions. In order to eliminate the effect of the asymmetry potential, the potential difference was measured by exchanging the electrodes in the two compartments and the average of the two values was calculated. The membrane potential E_m is defined as follows:

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

where R is the ideal gas constant, T is the absolute temperature, F is the Faraday constant, and c_2 and c_1 is the concentration of Cl^- ions in bulk solutions ($c_1 > c_2$), respectively.

Measurement of Surface Hydrophilicity of PES Membranes by Contact Angle Measurement

Surface hydrophilicity of the membranes was measured on a contact angle equipment with water as test liquid. Dried PES membranes with the size of 20 mm × 10 mm were measured on this equipment. The contact angle value for each profile of water sessile drop was accurately measured with an axisymmetric drop shape analysis (ADSA) software (8).

BSA Adsorption Amount on the Surface of PES Membranes

In order to measure the protein adsorption property on the surface of the membranes, BSA adsorption amount was measured through a static adsorption method. Three pH values were applied for the BSA solutions, which were 2.2, 4.8, and 8.0. The membrane with the area of 12.6 cm^2 was first ultrasonically treated in 30 mL of phosphate solution (PBS, 0.1 M) for 5 min. Then it was immersed in BSA phosphate solution (1.0 mg/mL) for 24 h at 25°C. After adsorption, the membrane was rinsed with PBS solution for three times and ultrasonically treated in PBS solution for 5 min to remove the adsorbed BSA (9,10). The amount of adsorbed BSA on the membrane was determined by measuring the BSA concentration in PBS by a UV-vis spectrophotometer (T6 New Century, Beijing, China).

Ultrafiltration Experiment

The ultrafiltration experiment was carried out on a self-made cross-flow equipment at 20°C. The concentration of BSA phosphate solution was 1.0 mg/mL. The transmembrane pressure was maintained at 100 kPa by nitrogen gas. The flow speed of the feed was 0.64 kg/h, which was controlled with a peristaltic pump. All membranes were pressed with water at 200 kPa for 30 min before measurements. Pure water permeation flux and rejection to BSA were measured after circulating for 5 min. Permeation flux, J_w ($\text{kg/m}^2 \cdot \text{h}$), was calculated by the following equation:

$$J_W = \frac{m}{At}$$

where m was the mass of permeation water, A was the membrane area (12.6 cm^2), and t was the permeation time. The rejection (R) was calculated by the following equation:

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

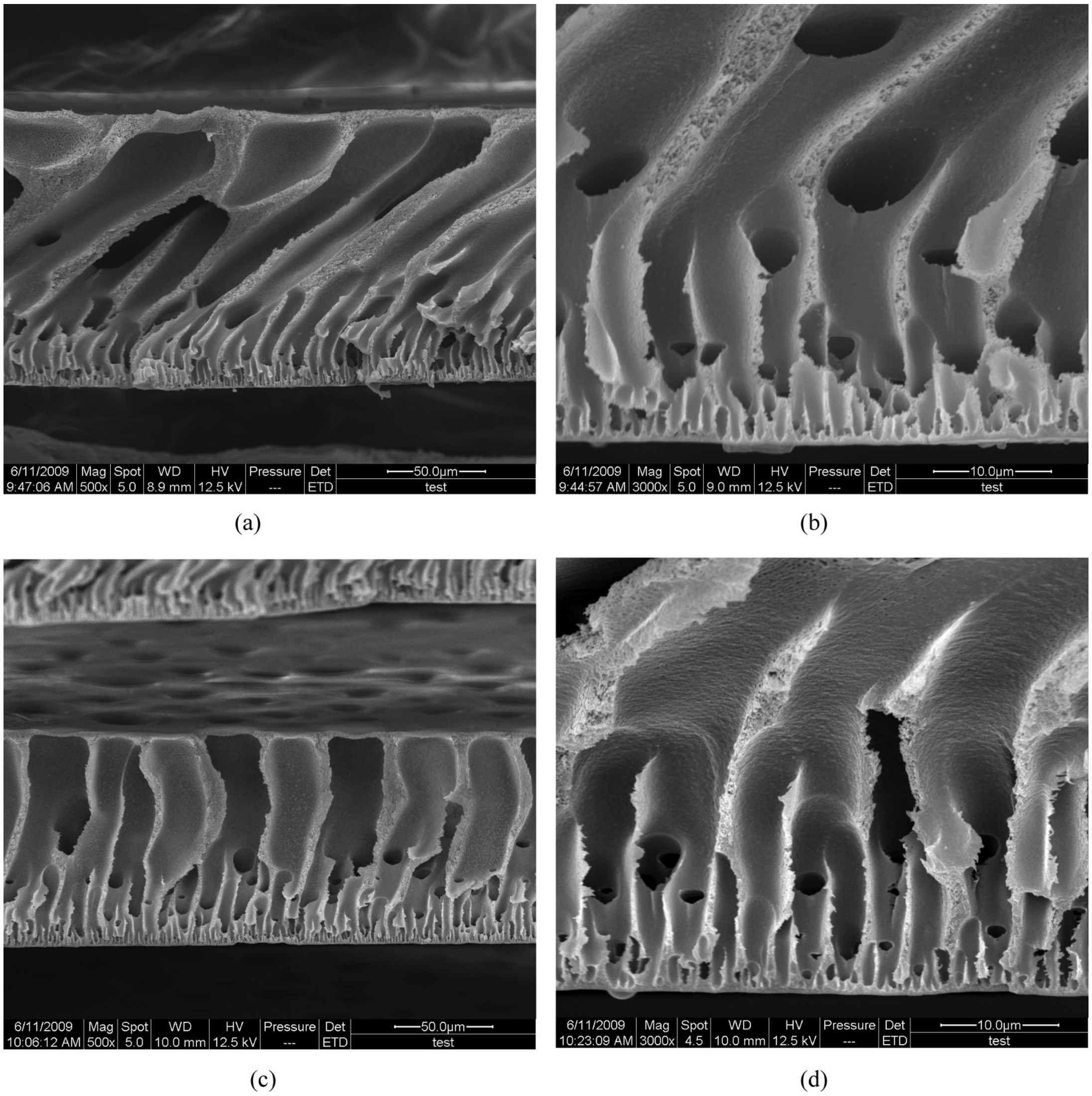
where C_p(mg/mL) and C_f (mg/mL) was the concentration of BSA in the permeation and feed side, respectively.

RESULTS AND DISCUSSION

Effects of External Voltage on Morphology and Surface Functional Groups of PES Membranes

Figure 2 shows the cross-section morphologies of two PES membranes, which were prepared at the conditions of 0 kV and 5 kV external voltages, respectively. It shows that the membranes have typical asymmetric structures, which consist of a thin skin layer and a porous sublayer. From the morphologies measured at 3000 X, it seems that there are no distinct differences in the membrane structures. Figure 3 shows the surface morphologies of the two membranes. It shows that the porosity density in the surface of 5 kV PES membrane is slightly less than the porosity density of 0 kV membrane. This will be further proved with their pure water fluxes of the ultrafiltration experiments. The surface roughness degree is also shown in Fig. 3. The surface of 5 kV PES membrane is slightly smoother than 0 kV PES membrane. The absolute roughness of the two surfaces is smaller than 10 nm. Consequently, the external voltage had no distinct effect on the cross-section structure, but had some effects on the surface morphology of the PES membranes. The phase inversion process of membrane formation is a very complicated process which is determined by both the particular thermodynamic interactions between the components and the kinetic factors. We speculate that the strong electric field would change the concentration of each component in the surface of the nascent membrane. In addition, the kinetic movement of the surface molecular chains or groups of the nascent membrane would also be partially confined when the nascent membrane was placed in the strong electric field during the phase inversion period. The two reasons simultaneously acted on the formation of the membrane surface structure. However, proving the above speculation will need more detailed research works.

Figure 4 shows the FTIR spectra of the PES membranes. The peak at 1648 cm^{-1} belongs to $C=O$ stretching in PVP. It shows that the relative intensity of the peak in 5 kV PES membrane is stronger than the peak in 0 kV PES membrane. Therefore, the relative content of carbonyl groups in the surface of the electric enhanced membranes



(a) (b)

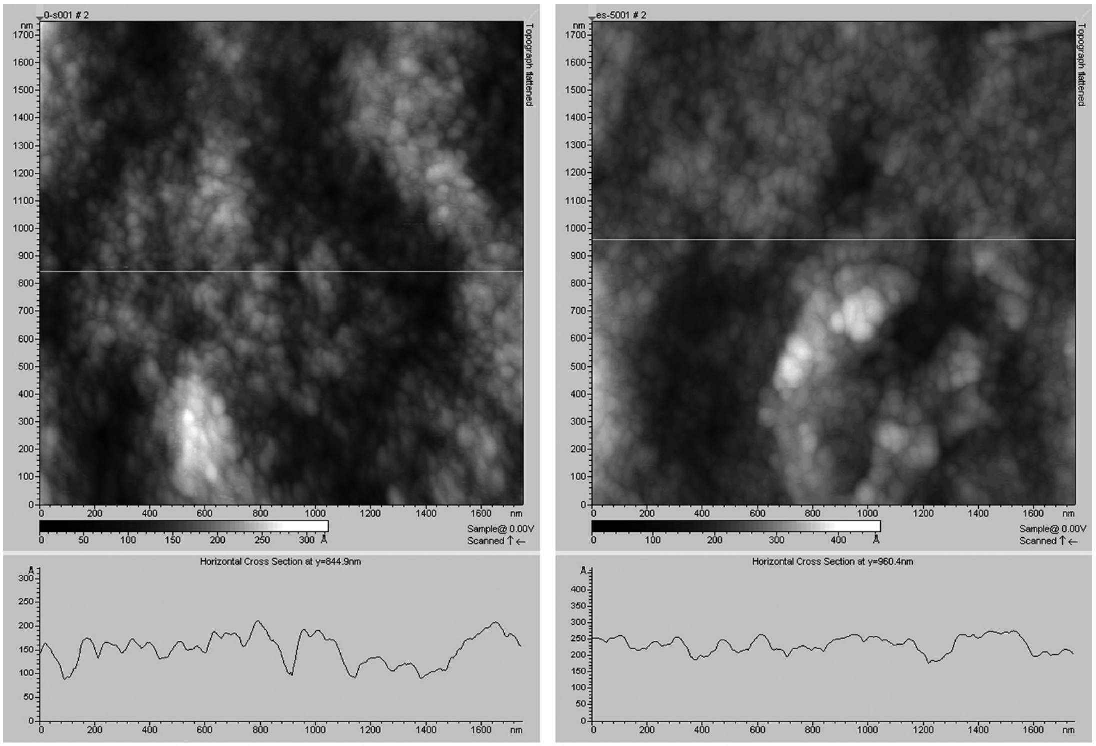
(c) (d)

FIG. 2. Cross-section morphologies of PES membranes; (a) 0 kV PES membrane, 500 X; (b) 0 kV PES membrane, 3000 X; (c) 5 kV PES membrane, 500X; (d) 5 kV PES membrane, 3000X.

was changed by the external voltage. Because the top electrode was a positive electrode, groups with high electron donor property, such as the carbonyl group in PVP molecules, were forced to move to the outer surface of the nascent membranes by the static electric force before the membranes were immersed in the coagulation. After the membranes were immersed in the coagulation, the phase inversion process happened soon, and the molecule chains of PES and PVP were unable to freely move anymore.

Effects of External Voltage on Membrane Potential, Surface Hydrophilicity, BSA Adsorption Amount, and Membrane Performances

Figure 5 shows the variation of membrane potential versus the logarithm of the concentration ratio $\ln(c_1/c_2)$ for 5 kV PES membrane. The concentration of KCl solution in compartment 2 (contacting with the bottom surface of the membranes) was kept constant at 1×10^{-3} mol/L. The figure shows that the membrane potentials are always negative at different pH solutions. For 0 kV membrane, it was found that the membrane potential was almost zero at any pH solutions. In the solution of $\text{pH} = 7.0$, the negative membrane potential meant that negative charges existed at the top surface of the 5 kV membrane. Because a positive electric field was formed during the preparation of membranes, negative charges (e.g., carbonyl groups, as the explanation for Fig. 4) would be permanently held at the top surface of the prepared membranes. An explanation on why negative membrane potential existed in acidic solutions needs further research works.



(a) (b)

FIG. 3. Surface morphologies of PES membranes; (a) 0 kV PES membrane; (b) 5 kV PES membrane.

The surface hydrophilicity of the PES membranes was also distinctly changed by the external voltage which was proved with the contact angle values of water listed in Table 1. When the external voltage increased, the contact angles of water decreased. It meant that the surface hydrophilicity of the membranes increased when external high voltage was applied. Table 1 also lists the pure water flux of the membranes. It shows that all of the fluxes are higher than $130\,\mathrm{kg/m^2 \cdot h}$. Although the surface hydrophilicity increased with the external voltages, the flux slightly decreased with the external voltages. The reason was that the UF membrane was a pressure driven process. The flux was largely influenced by the pressure and porosity density. Because the surface porosity density decreased when external high voltage was applied as shown in Fig. 3, the flux decreased with the increase of the external voltages.

The effect of the external voltage on BSA adsorption amount of the membranes was observed through the static adsorption experiment. Figure 6 shows the BSA adsorption amounts at three pH conditions. It shows that BSA adsorption amounts distinctly change with the external voltages. BSA is a protein which is composed of many amino acids. The isoelectric point (IEP) for BSA appears when pH is 4.8 (11). When the pH value is higher than 4.8, BSA molecules show negative potential. On the contrary, when the pH value is lower than 4.8, BSA molecules show positive potential. Therefore, in the basic solution ($\mathrm{pH} = 8.0$), the BSA adsorption amounts decreased with the increase of the voltages because a negative-negative electrostatic repulsive force existed between the surface of the membranes and BSA molecules, and the repulsive forces became strong when the external voltages increased. In the acidic solutions (e.g., $\mathrm{pH} = 2.2$), because higher negative potential existed at the surface of the membranes as illustrated in Fig. 5, a negative-positive attractive force existed between the membranes and BSA. Consequently, the BSA adsorption amounts increased in the acidic solutions.

Figure 7 shows the effect of external voltages on the rejection to BSA. It shows that in the basic solution ($\mathrm{pH} = 8.0$), the rejection is larger than 90%, but in the acidic solution ($\mathrm{pH} = 2.2$), the rejection is lower than 70%. This phenomenon was still the result of the electric charge interactions as discussed on the BSA adsorption amounts. However, for each BSA solution, the change of rejection with the external voltages was not large. The reason was that the average pore size and porosity density of the membranes did not change with the external voltages. Consequently, only the pH value had a big influence on the rejection.

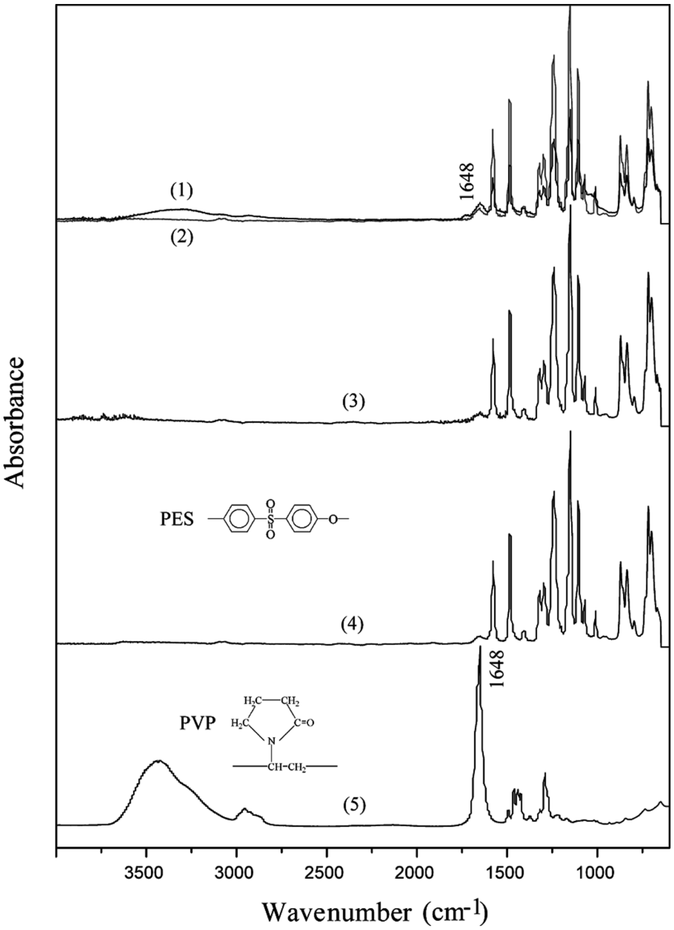


FIG. 4. FTIR spectra of PES membranes; (1) ATR-FTIR spectra of top surface of 5 kV PES membrane; (2) ATR-FTIR spectra of top surface of 0 kV PES membrane; (3) ATR-FTIR spectra of top surface of PES membrane (without adding PVP); (4) FTIR spectra of PES homogeneous film (without adding PVP); (5) FTIR spectra of PVP 30 K (KBr disk).

TABLE 1
Contact angle of water on PES membranes, and pure water flux of PES membranes

Voltage (kV)	Contact angle (°) of water	Pure water flux ($kg/m^2 \cdot h$)
0	72.3 ± 0.1	149.3 ± 0.5
1	68.8 ± 0.1	134.9 ± 0.4
2	68.2 ± 0.1	142.3 ± 0.4
3	67.1 ± 0.1	129.8 ± 0.3
4	66.2 ± 0.1	137.6 ± 0.5
5	64.3 ± 0.1	134.9 ± 0.4

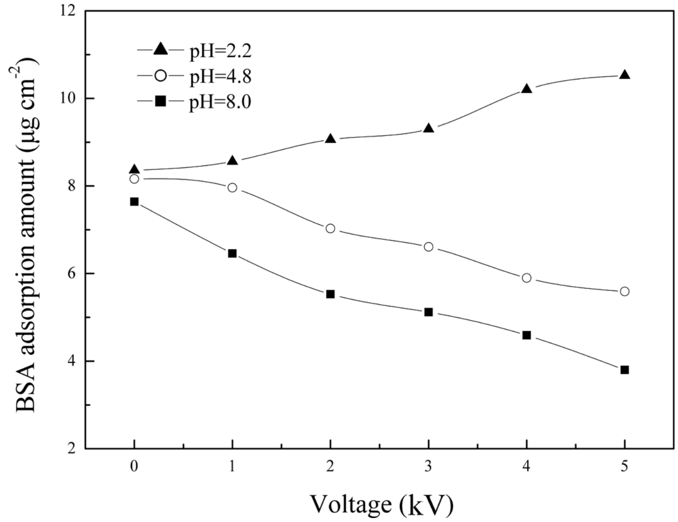


FIG. 6. BSA adsorption amount on PES membranes vs. external voltage.

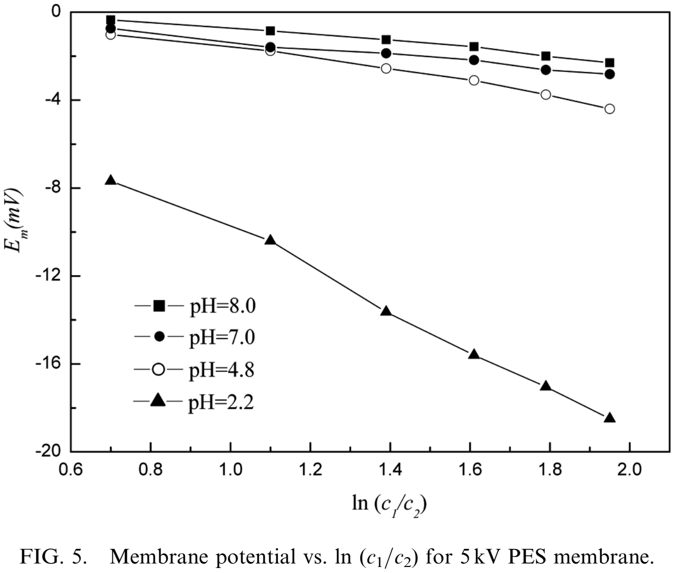


FIG. 5. Membrane potential vs. ln (c_1/c_2) for 5 kV PES membrane.

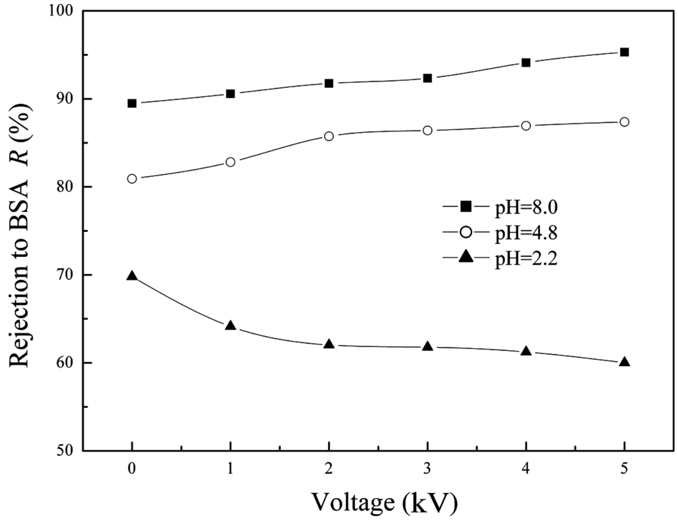


FIG. 7. Rejection to BSA of PES membranes vs. external voltage.

CONCLUSION

In this study, the novel method of applying high voltage (1–5 kV) to the conventional immersion precipitation phase inversion process was used to prepare anti-fouling PES ultrafiltration membranes when PVP (30 K) was used as an additive. It was found that the external electric field distinctly influenced the surface functional groups (such as carbonyl groups in PVP), surface hydrophilicity, and membrane potential of the membranes. With the increase of the external voltage, the surface hydrophilicity and the membrane potential decreased. The external voltage had no influence on the cross-section structure of the membranes, but the surface porosity density slightly reduced when the external voltage increased. In basic BSA solution, the protein adsorption amount on the enhanced membranes was distinctly reduced when comparing with the un-enhanced membrane, and the rejection was improved. Consequently, the prepared PES membranes had distinctive anti-fouling properties.

ACKNOWLEDGEMENTS

The authors acknowledge the financial supports by National Natural Science Foundation of China (20906010).

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