

# Antifouling property improvement of poly(vinyl butyral) ultrafiltration membranes through acid treatment

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## Abstract

PVB ultrafiltration membranes were first prepared via the well-known phase inversion process, and then treated with HCl to improve their antifouling property. Water contact angle measurement indicated the remarkable increase of membrane surface hydrophilicity, X-ray photoelectron spectroscopy (XPS) confirmed the hydrolysis of butyral groups within the membrane, and scanning electron micrograph (SEM) suggested that acid-treated membranes preserved asymmetric structure. Ultrafiltration results showed that separation performance and antifouling property of PVB membranes were considerably affected by acid treating conditions. Prolonging treating time or increasing HCl concentration could increase surface hydrophilicity effectively and thus render the membranes better antifouling property.

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**Keywords:** Poly(vinyl butyral) membrane; Acid treatment; Ultrafiltration; BSA; Antifouling property

## 1. Introduction

As an environment-friendly, bio-compatible, and energy-efficient separation technology, ultrafiltration has been widely applied for the recovery of bioproducts from aqueous solutions. However, the serious fouling, caused by the adhesion or deposition of biomolecules on the membrane surface and the entrapment or aggregation of biomolecules inside the pores, brings a great loss of separation performance and becomes a bottleneck for industrial application [1]. Many researches have indicated that membrane fouling was greatly related to the surface property, especially hydrophilicity; the common strategy to suppress protein fouling was to effectively reduce protein adsorption and deposition on the membrane through creating highly hydrophilic surface [2–6].

Most ultrafiltration membranes utilized nowadays are hydrophobic, and many efforts have been devoted to the surface modification with hydrophilic materials to enhance hydrophilicity and consequently antifouling property of the membranes [7–12]. On the other hand, some hydrophilic membranes, such as poly(vinyl alcohol) (PVA)-based membrane, have also been

prepared to resist protein fouling [5,6,13–18]. PVA is a highly hydrophilic, nontoxic, and biocompatible polymer with excellent mechanical strength, thermal stability, and pH stability [19]. However, in the phase inversion process of PVA membrane, the diffusion of solvent and coagulant is much slower than that of hydrophobic membranes, resulting in a much denser skin layer and an extremely lower flux [15,16]. Thus, PVA was rarely used for the preparation of ultrafiltration membrane directly. In order to improve the separation performance, hydrophobic groups can be tentatively introduced to accelerate the diffusion of solvent and coagulant during PVA membrane preparation [18].

The introduction of butyral groups into PVA can be achieved through an acid catalyzed reaction between PVA and butyraldehyde. The reaction product poly(vinyl butyral) (PVB) contains hydrophobic butyral groups and hydrophilic hydroxyl groups. Since PVA is generally obtained from the hydrolysis of polyvinyl acetate [20], there will also be a quite limited amount of residual acetate groups in PVB molecules. Recently, PVB ultrafiltration membranes have been successfully prepared and membrane preparation conditions have been discussed in detail [21–25]. The skin layer formation of PVB membrane from different solvents was determined by the combination of the equilibrium thermodynamics and membrane formation kinetics, whereas, the sub-layer of the membrane was dominated by the diffusion rate of solvent–nonsolvent [23].

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Based on the earlier studies, a further investigation will be taken in this study on the antifouling property of PVB membranes, which is greatly dependent on the surface hydrophilicity. Since the increase of hydroxyl groups will effectively increase the hydrophilicity, we can thus imagine that converting some butyral groups and acetate groups in PVB chains into hydroxyl groups will surely improve the antifouling property of PVB membranes.

In the present study, PVB membranes were prepared through a phase inversion method in a wet process, and the pristine membranes were then treated with HCl solution under different treating time and HCl concentration. Hydrophilicity of PVB membranes was evaluated by contact angle measurement, surface and cross-section morphologies were observed by scanning electron microscope (SEM), and surface chemical composition was analyzed by X-ray photoelectron spectroscopy (XPS). The effect of treating time and HCl concentration on separation performance and antifouling property of PVB membranes was investigated through ultrafiltration experiments using bovine serum albumin (BSA) as a model protein.

## 2. Experimental

### 2.1. Materials

PVB was kindly supplied by Huida Chemical Industry Co. Ltd. (Tianjin, China) with an average polymerization degree of 1700. Vinyl butyral and vinyl alcohol parts of the polymer were 81 and 14 wt%, respectively. The residual vinyl acetate part was 5 wt%. *N,N*-dimethyl acetamide (DMA) was purchased from Damao Chemical Reagent Co. (Tianjin, China). Bovine serum albumin (BSA) was purchased from Institute of Hematology, Chinese Academic of Medical Sciences (Tianjin, China). All other chemicals were of analytical grade.

### 2.2. Membrane preparation

PVB membranes were fabricated through an immersion-precipitation method. Casting solution was prepared by dissolving PVB in DMA with rigorous stirring at 60 °C. Then the solution was cast on a glass plate and immediately immersed into a deionized water bath with a temperature of 20 ± 1 °C. Pristine membranes were obtained within a few minutes and washed thoroughly with deionized water. The membranes were then post-treated by immersing into HCl solution for a given time.

### 2.3. Characterization of membranes

The static contact angle was measured with a contact angle goniometer (Erma Contact Angle Meter, Japan). Membranes were dried and pressured to obtain dense films before each measurement in order to eliminate the effect of capillary penetration. The surface and cross-sectional morphologies were observed by SEM (Philips XL30E scanning microscope). Membranes were frozen in liquid nitrogen, broken, and sputtered with gold before SEM analysis. The porosity ( $\rho$ ) of the membrane was also tested,

which was calculated by the following equation:

$$\rho = \frac{W_1 - W_2}{W_1} \quad (1)$$

where  $W_1$  and  $W_2$  were the weight of the wet and dry membrane, respectively, which could be obtained by weighing a piece of membrane before and after fully dried under vacuum. The chemical composition of membrane surface was analyzed by XPS (PHI-1600, USA) using Mg K $\alpha$  (1254 eV) as radiation source (the take-off angle of the photoelectron was set at 90°). Survey spectra were collected over a range of 0–1100 eV and high-resolution spectra of C1s were collected over a range of 280–292 eV. The mechanical property was tested with a material-testing machine (AXM350-10KN, Testometric Co., UK). Prior to test, membranes were dried and cut into rectangle strips with a dimension of 30 mm × 10 mm (length × width). The stress–strain curve was obtained at an extension rate of 9 mm/min, from which the tensile strength, elastic modulus, and maximum elongation of the membranes were determined.

### 2.4. Ultrafiltration experiments

Ultrafiltration experiments were carried out using a dead-end stirred cell filtration system (Model 8200, Millipore Co., USA) connected with a N<sub>2</sub> gas cylinder and solution reservoir. The operating pressure was maintained by N<sub>2</sub> gas. All the ultrafiltration experiments were carried out at a stirring speed of 400 rpm and a temperature of 20 ± 1 °C.

After the membrane was fixed, the stirred cell and the solution reservoir were filled with deionized water. The membrane was first pressurized under a high pressure of 150 kPa for 30 min, then the pressure was reduced to the operating pressure of 100 kPa and the water flux ( $J_{w1}$ ) was measured. After 30 min filtration, the feed solution was switched to 1.0 mg/ml BSA phosphate buffer saline (0.1 M, pH 7.0), and the BSA solution flux ( $J_p$ ) was measured. Finally, the cell and the solution reservoir were fully emptied and refilled with deionized water. The membrane was cleaned in the stirred cell with deionized water for 20 min, and the water flux ( $J_{w2}$ ) was measured again.

The water flux of the membrane was calculated by the following equation:

$$J_w = \frac{V}{A \Delta t} \quad (2)$$

where  $V$  was the volume of permeated water (l),  $A$  the membrane area (m<sup>2</sup>) and  $\Delta t$  was the ultrafiltration time (h). The BSA rejection ratio,  $R$ , was defined as follows:

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

where  $C_p$  and  $C_f$  (mg/ml) were BSA concentrations of permeate and feed solutions, respectively. The flux loss ratio ( $R_l$ ) and the flux recovery ratio ( $R_r$ ) were introduced to describe the antifouling property of the membrane.  $R_l$  and  $R_r$  were defined by the

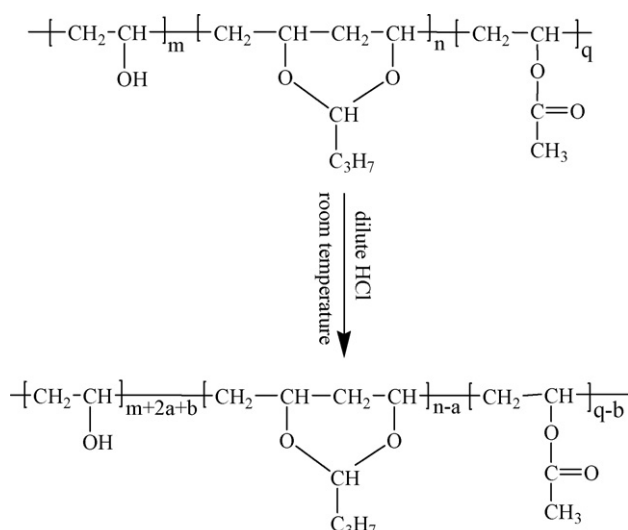


Fig. 1. Schematic illustration of HCl catalyzed hydrolysis reaction of PVB.

following equations:

$$R_1 (\%) = \left( 1 - \frac{J_p}{J_{w1}} \right) \times 100 \quad (4)$$

$$R_r (\%) = \frac{J_{w2}}{J_{w1}} \times 100 \quad (5)$$

where  $J_{w1}$  and  $J_p$  ( $l/m^2 h$ ) were the steady flux of water and protein solution for the fresh membrane, and  $J_{w2}$  ( $l/m^2 h$ ) was the steady water flux for the cleaned membrane.

### 3. Results and discussion

#### 3.1. Characterization of acid-treated membranes

The separation performance of PVB membranes was greatly influenced by membrane preparation conditions. It was found that PVB membranes had a lower water flux and a higher rejection ratio when PVB concentration was increased in the casting solution or the coagulation temperature was increased [23]. In our study, we chose a PVB concentration of 13 wt% and a coagulation temperature of 20 °C for PVB membrane preparation, and an asymmetrical structure was successfully obtained. Acid treatment was actualized with different treating time and HCl concentration. The hydrolysis reaction catalyzed by HCl was schematically shown in Fig. 1.

Water contact angle was measured to evaluate the surface hydrophilicity of PVB membranes. Fig. 2 presented the contact angle of the membranes with different treating time and HCl concentration, respectively. Each data in Fig. 2 was an average of five readings. It could be seen that the control PVB membrane had the highest contact angle, which indicated the lowest hydrophilicity. The contact angle of acid-treated membranes was decreased with prolonged treating time or increased HCl concentration, suggesting that more butyral groups in PVB had been replaced by hydroxyl groups and the surface hydrophilicity was increased correspondingly.

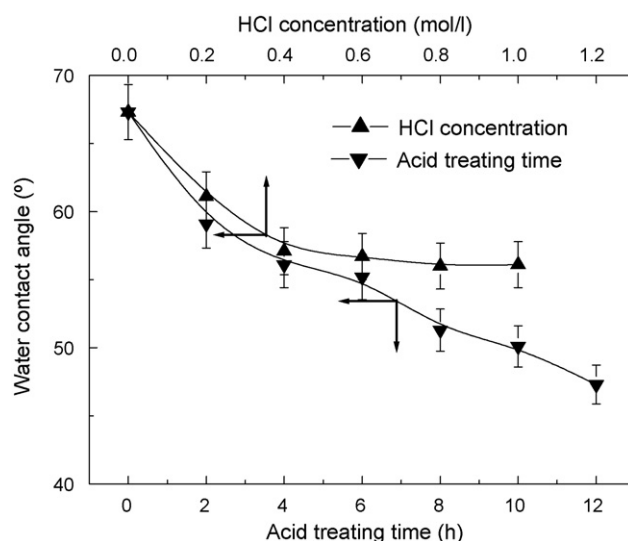


Fig. 2. Contact angle of acid-treated PVB membranes as a function of acid treating time and HCl concentration.

The surface and cross-sectional morphologies of control and acid-treated PVB membranes were given in Fig. 3. The surface morphology of the membrane after 12 h treatment in 1 M HCl was similar to that of the control membrane. Meanwhile, all the membranes exhibited the typical structure of ultrafiltration membranes consisting of a top layer with a dense structure, an intermediate layer with a finger-like structure, and a bottom layer with fully developed macropores. There were no significant morphological variations after acid treatment, which indicated that HCl treatment did not remarkably alter the structure of PVB membrane. The porosity of control and acid-treated PVB membranes was measured and the results were shown in Table 1. All the membranes had an approximate porosity between 84 and 87%, which meant that acid treatment had no remarkable influence on the porosity of PVB membrane.

Surface composition of control and acid-treated PVB membranes was analyzed by XPS to confirm the hydrolysis of butyral groups. As shown in Fig. 4, the C1s peak in the spectra was composed of an alkyl carbon peak ( $-C-C-$ ), an ether carbon peak ( $-C-O-$ ) and a carbonyl carbon peak [ $-(C=O)-$ ], which were observed at 284.5, 285.9 and 287.9 eV, respectively [26]. The area percent of each peak was calculated and a decrease of the alkyl carbon peak from 67.4 to 59.8 mol% after 12 h HCl treatment was observed, indicating the release of some butyral groups and the increase of hydroxyl groups. XPS results were consistent with the increased hydrophilicity of membrane surface observed by water contact angle measurement. On the other hand, the decreased carbonyl carbon peak intensity from 5.6 to 3.8 mol% was due to the hydrolysis of acetate groups at PVB chains [20].

The mechanical property of membranes was of great importance for practical application. Table 1 presented maximum strength, elastic modulus, maximum elongation and thickness of all the membranes. All the parameters of mechanical property were slightly changed in a limited range, which indicated that acid treatment had no distinct influence on the mechanical property of PVB membranes, and all the membranes could well

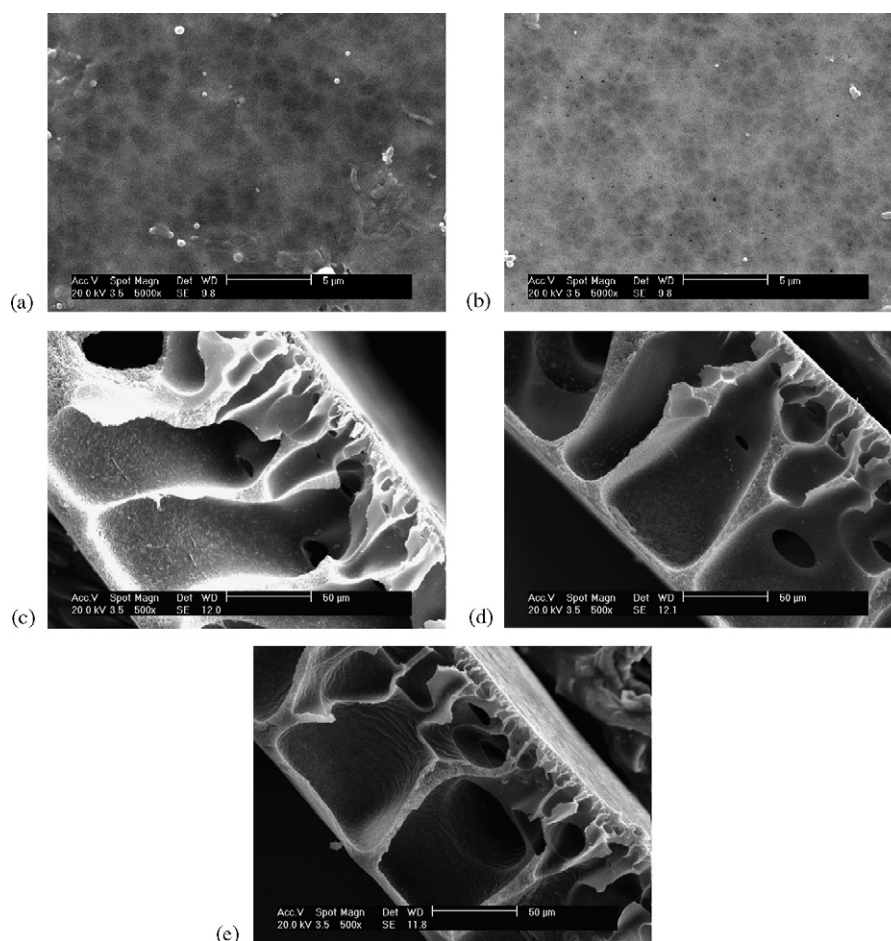


Fig. 3. Surface morphology of (a) control PVB membrane and (b) membrane treated for 12 h in 1.0 M HCl; cross-sectional SEM morphology of (c) control PVB membrane, (d) membrane treated for 4 h in 0.2 M HCl and (e) membrane treated for 12 h in 1.0 M HCl.

meet the requirements for actual ultrafiltration in the present work.

### 3.2. Effect of acid treating time on membrane separation performance and antifouling property

Even if PVB membranes were basically regarded as hydrophilic membranes, the hydrophobic butyral groups would

cause a great loss of antifouling property. As mentioned before, it was anticipated that the antifouling property of PVB membranes could be improved through acid treatment.

Fig. 5 showed the effect of treating time on the separation performance of acid-treated membranes (HCl concentration was kept at 1.0 M). When the treating time was prolonged from 0 to 6 h, the pure water flux of PVB membrane was dropped from 68.0 to 26.8 l/m<sup>2</sup> h. However, it had a significant increase from

Table 1  
Porosity and mechanical property of acid-treated membranes with different treating time and HCl concentration

Membrane	Treating time (h)	HCl concentration (mol/l)	Porosity (%)	Young's modulus (MPa)	Maximum elongation (%)	Maximum strength (MPa)	Membrane thickness ( $\mu\text{m}$ )
1#	0	0	86.05	52.75	46.56	1.92	191
2#	2	1.0	86.07	48.66	48.50	1.96	205
3#	4	1.0	86.97	52.22	50.98	1.88	177
4#	6	1.0	85.76	61.17	52.71	2.06	198
5#	8	1.0	84.85	60.73	57.68	2.04	195
6#	10	1.0	85.46	59.23	59.79	2.14	188
7#	12	1.0	84.84	58.48	53.18	2.25	194
8#	4	0.2	86.30	55.35	51.12	1.96	196
9#	4	0.4	85.62	51.52	56.70	2.05	203
10#	4	0.6	85.80	55.71	54.86	2.02	202
11#	4	0.8	86.10	51.41	50.87	2.09	189
12#	4	1.0	86.97	52.22	50.98	1.88	177

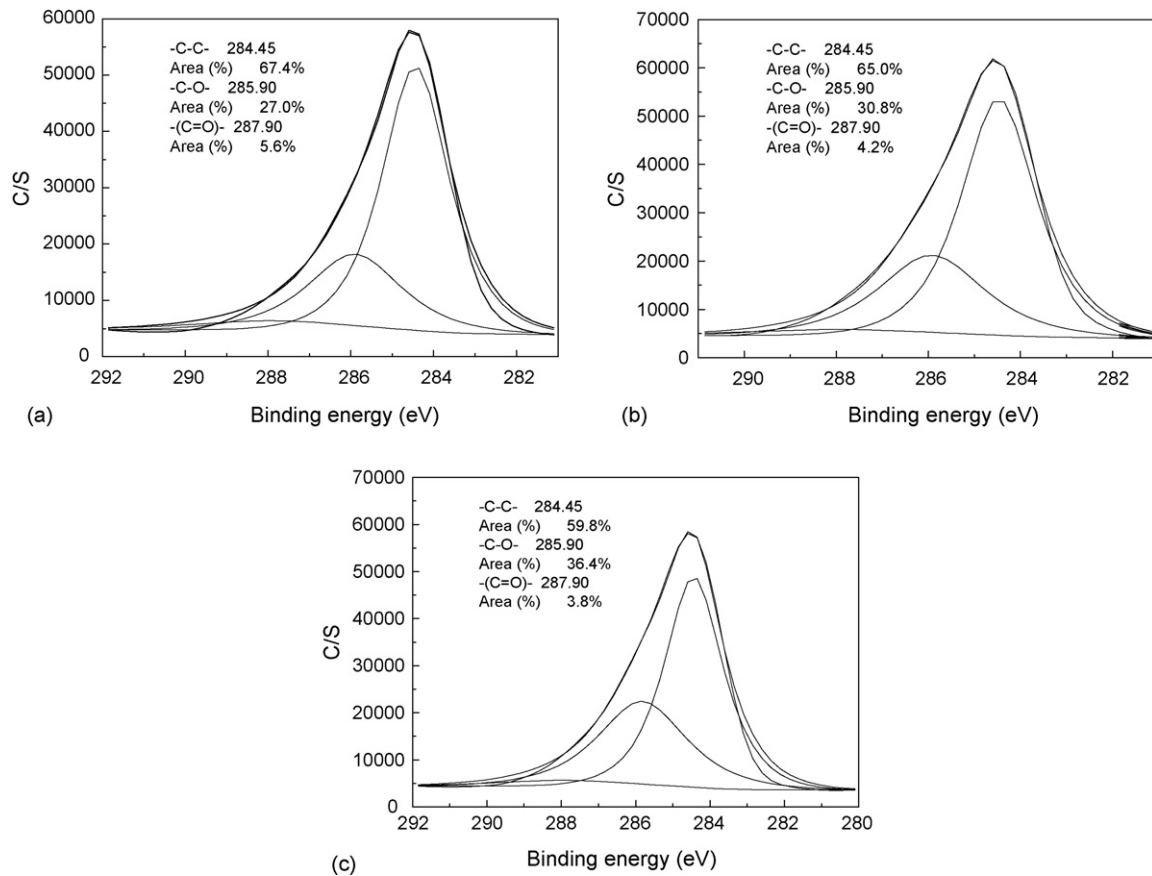


Fig. 4. XPS spectra of C<sub>1s</sub> for control PVB membrane (a), membrane treated for 4 h in 0.2 M HCl (b) and membrane treated for 12 h in 1.0 M HCl.

26.8 to 79.5 l/m<sup>2</sup> h when the treating time was further prolonged from 6 to 12 h.

Water flux was related to the pore size in the skin layer of membranes. In PVB membranes, hydrophobic interaction existed between PVB chains through butyral groups. After acid treatment, some butyral groups at the membrane surface were hydrolyzed, so that the hydrophobic interaction was reduced and PVB chains were undertaken structural rearrangement. The swelled chains around the pores in the skin layer resulted in a

decrease of pore size and correspondingly a flux decline. Meanwhile, since PVA was highly hydrophilic, it was reasonable to assume that some of the chains could be dissolved in water and fall off from the membrane surface, leading to the appearance of bigger pores in the skin layer, and the flux was consequently increased. For a short acid treating time from 0 to 6 h, the former effect was the dominant factor and the appearance of bigger pores had slight influence on flux. However, when treating time was further prolonged, more bigger pores appeared in the skin layer and the latter effect became dominant, thus the flux was increased.

BSA was used as a model protein to investigate the separation performance and antifouling property of acid-treated PVB membranes. The rejection ratio was declined from 68.0 to 23.2% within the treating time range. Although the decrease of pore size would result in some increase of rejection ratio, the appearance of bigger pores was the dominant factor which made the rejection ratio decrease. Along with the prolonged treating time, the amount of bigger pores was increased and the rejection ratio was further decreased.

The flux decline during the ultrafiltration of BSA solution ( $J_p$  was smaller than  $J_{w1}$ ) was usually attributed to membrane fouling and concentration polarization. Considering the high molecular weight of BSA and rigorous stirring near the membrane surface, concentration polarization could be minimized; it was thus assumed that the flux decline was mainly caused by protein fouling in the present study. Flux loss ratio and flux

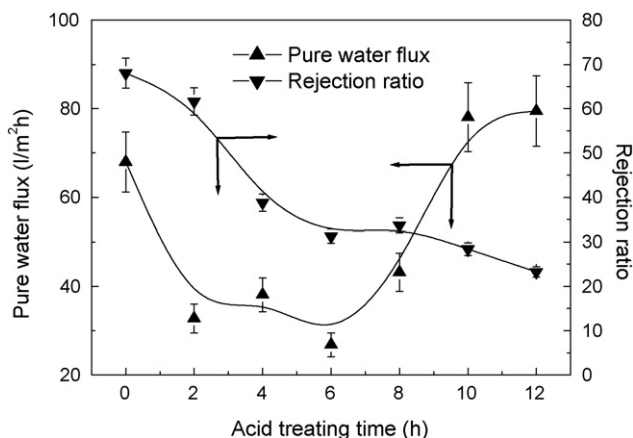


Fig. 5. Effect of acid treating time on the separation performance of acid-treated membranes.

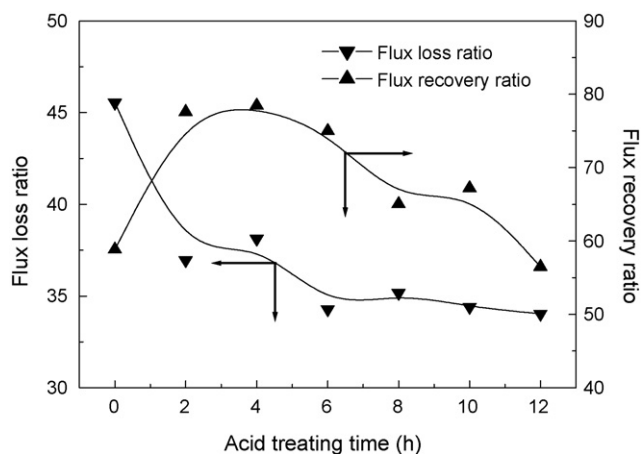


Fig. 6. Effect of acid treating time on the antifouling property of acid-treated membranes.

recovery ratio were employed to evaluate the antifouling property of PVB membranes. A lower flux loss ratio meant a less serious fouling, while a higher flux recovery ratio meant a better recycling ability.

Fig. 6 presented the effect of acid treating time on the membrane antifouling property. The flux loss ratio was decreased from 45.5 to 34.3% and the flux recovery ratio was increased from 58.8 to 75.0% when treating time was prolonged from 0 to 6 h, which indicated that the antifouling property of PVB membranes was gradually improved. The increased hydroxyl groups after acid treatment would make the membrane surface more hydrophilic, and this PVA-like surface exhibited excellent protein resistance [27]. When the acid treating time lasted for longer than 6 h, a great number of bigger pores appeared in the skin layer; BSA molecules might be entrapped inside these bigger pores and could not be removed only through water cleaning, resulting in the drop of flux recovery ratio. But the flux loss ratio changed slightly due to the substantial improvement of hydrophilicity on the membrane surface.

### 3.3. Effect of HCl concentration on membrane separation performance and antifouling property

The effect of HCl concentration on the separation performance of PVB membranes was shown in Fig. 7. The treating time for all HCl concentrations was 4 h. Pure water flux was decreased from 68.0 to 38.1 l/m<sup>2</sup> h and BSA rejection ratio was also decreased from 68.0 to 38.8% with an increase of HCl concentration from 0 to 1.0 M. Swelling and leaving of the hydrolyzed PVB polymer around the pores in the skin layer of PVB membranes could also be used to explain the effect of HCl concentration on the membrane performance.

Fig. 8 presented the antifouling property of PVB membranes treated with different HCl concentration. Flux loss ratio was decreased from 45.5 to 38.1% and flux recovery ratio was increased from 58.8 to 78.5% with an increase of HCl concentration from 0 to 1.0 M. When the membranes were treated with higher HCl concentration, the hydrolysis reaction was accel-

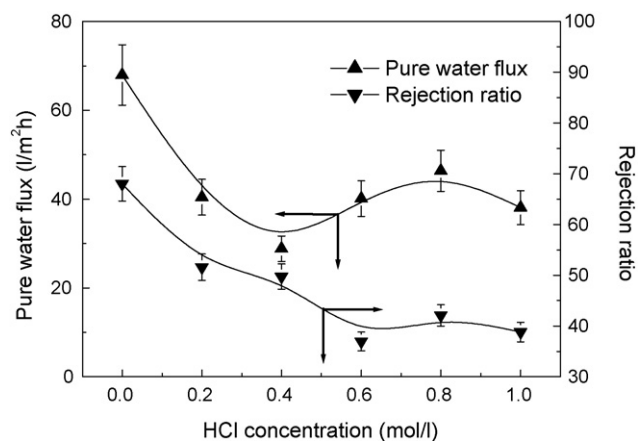


Fig. 7. Effect of HCl concentration on the separation performance of acid-treated membranes.

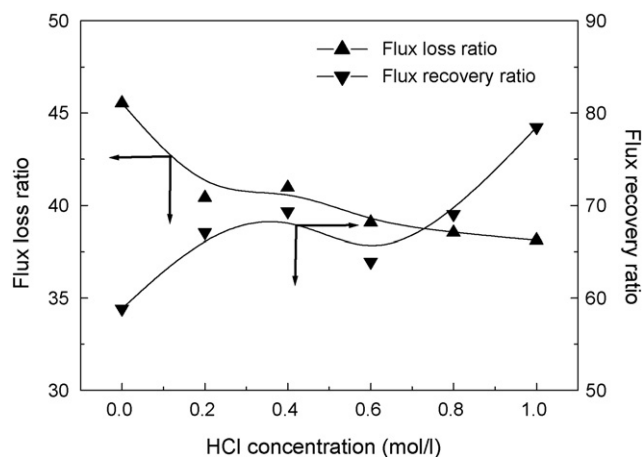


Fig. 8. Effect of HCl concentration on the antifouling property of acid-treated membranes.

erated, more butyral groups were released, and the membrane surface became more hydrophilic, so that a better antifouling property of membrane was achieved.

## 4. Conclusions

In this study, PVB ultrafiltration membranes were successfully fabricated and the antifouling property of the membranes was improved through acid treatment, as some of the butyral groups at membrane surface were hydrolyzed and converted to hydrophilic hydroxyl groups in the acid treatment. Ultrafiltration experiments indicated the improved antifouling property of the PVB membranes after acid treatment. When the treating time was prolonged to 6 h at an HCl concentration of 1.0 mol/l, the flux loss ratio of PVB membrane was decreased from 45.5 to 34.3% and the flux recovery ratio was increased from 58.8 to 75.0%; when the HCl concentration was increased to 1.0 mol/l for a treating time of 4 h, the flux loss ratio was decreased from 45.5 to 38.1% and the flux recovery ratio was increased from 58.8 to 78.5%.

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