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# Preparation and performance of cellulose acetate/polyethyleneimine blend microfiltration membranes and their applications

Zhaoan Chen<sup>a,b,\*</sup>, Maicun Deng<sup>a,b</sup>, Yong Chen<sup>a,b</sup>, Gaohong He<sup>a,c</sup>, Ming Wu<sup>a,b</sup>, Junde Wang<sup>b</sup>

<sup>a</sup> National Engineering Research Center of Membrane Technology, 457 Zhongshan Road, Dalian 116023, China
<sup>b</sup> Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China
<sup>c</sup> School of Chemical Engineering, Dalian University of Technology, Dalian 116012, China

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#### Abstract

A modified microfiltration membrane has been prepared by blending a matrix polymer with a functional polymer. Cellulose acetate (CA) was blended with polyethyleneimine (PEI), which was then crosslinked by polyisocyanate, in a mixture of solvents. In the membrane, PEI can supply coupling sites for ligands in affinity separation or be used as ligands for metal chelating, removal of endotoxin or ion exchange. The effects of the time of phase inversion induced by water vapor, blended amount of PEI and amount of crosslinking agent on membrane performance were investigated. The prepared blend membranes have specific surface area of  $12.04-24.11 \text{ m}^2/\text{g}$  and pure water flux (PWF) of  $10-50 \text{ ml/cm}^2$  min with porosity of 63-75%. The membranes, made of 0.15 50 wt.% PEI/CA ratio and 0.5 crosslinking agent/PEI ratio, were applied to adsorbing Cu<sup>2+</sup> and bovine serum albumin (BSA) individually. The maximum adsorption capacity of Cu<sup>2+</sup> ion on the blend membrane is 7.42 mg/g dry membrane. The maximum adsorption capacities of BSA on the membranes with and without chelating Cu<sup>2+</sup> ion are 86.6 and 43.8 mg/g dry membrane, respectively.

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### 1. Introduction

Rapid developments in biotechnology and the pharmaceutical potential of biomolecules have brought great demand for reliable, efficient methods to purify preparative amounts of proteins, peptides and nucleic acids [1–3]. Membrane filtration can meet the demand and is used in bioprocess recovery to remove cell debris, colloidal or suspended solids and virus particles from homogenized suspensions of bacterial cells [2]. In recent years, polymeric membrane materials with functional groups have gained more attention because through chemical modification, ligands intended for affinity, pseudo-affinity, ion exchange, etc. can be coupled to functional groups in membrane substrates to adsorb biomolecules selectively in the filtrate [2–4]. Thus, modified membrane is

\* Corresponding author. Tel.: +86-411-4379223;

fax: +86-411-4677947.

E-mail address: zachen@dicp.ac.cn (Z. Chen).

called as adsorptive membrane or membrane adsorber. Adsorptive membrane chromatography reflects technological advances in both membrane filtration and fixed-bed liquid chromatography. Dissolved molecules are carried directly to adsorptive sites in these membranes by convective flow, eliminating the long diffusion time required by resin-based chromatography. This adaptation increases the throughput of adsorption processes [5].

Based on the analysis of the adsorption kinetics [6–9], basic membranes should have homogeneously microporous/macroporous structure with a large internal surface area, high interconnectivity and mechanical stability, which is usually owed to the feature of microfiltration membrane. Adsorptive membrane substrates should be mechanically resilient and resistant to solvents used to activate coupling and not participate in secondary hydrophobic adsorption, which produces non-specific retention that interferes with product resolution or can lead to the denaturation of biopolymers. Most of the polymers used in manufacturing of microfiltration membranes, such as nylon [10-12], polysulfone [13,14] or polyethylene [15], display undesirable surface characteristics leading to strongly non-specific adsorption of proteins on the membrane surfaces. So it is needed to further modify the membranes to improve hydrophilicity of their surface and reduce the non-selective adsorption of proteins. Cellulose acetate (CA) is a popular substrate for adsorptive membranes with hydrophilic surfaces and low non-specific protein binding. However, membranes have to be deacetylated to obtain reactive hydroxyl groups with pore size changed and loss of rigidity [16]. Among reactive groups such as hydroxyl group, amine group and sulfhydryl group, amine groups and sulfhydryl groups are much more active than hydroxyl groups and can be much more easily attacked by modifying agents (which provide functional groups) under mild conditions [17,18]. Polyethyleneimine (PEI) is a branched chain polymer with a lot of amine groups and has extensively been used to modify membrane surface [19], effectively complex heavy metal ions [20-23] and selectively adsorb endotoxins [24] from protein solutions. By different methods of chemical modification, PEI can be immobilized on the surfaces of basic membranes and used as ligands [25-28] or to supply further coupling sites for immobilization of different ligands [29].

In this study, we developed a blend method to prepare a modified microfiltration membrane directly, which combines the properties of CA in membrane formation, such as high consistency of the pore size distribution and mechanical rigidity, and the properties of PEI such as chemical reactivity and capability of selectively adsorbing biological macromolecules. The method can simplify procedures of preparing adsorptive membranes and the amine groups of PEI blended in membranes make further modification easy under mild conditions. Thus, we can overcome shortcomings such as change of pore size and loss of rigidity coming from multiple steps under harsh conditions during the modification of commercial polymer membranes. The effects of polymer composition, water vapor induced time, amount of crosslinking agent on membrane performance were investigated. Copper ion and bovine serum albumin (BSA) were employed as model solutes to determine individually adsorption properties of metal ions and proteins onto CA/PEI blend membranes.

# 2. Experimental

# 2.1. Materials

Cellulose diacetate, HB-105 was obtained from Hoechst Celanese (Rock Hill, USA) and dried at 120 °C under vacuum over 8 h. Polyethyleneimine ( $M_n = 60\,000$ , ratio of primary amine, secondary amine and tertiary amine: 1/2/1), 50 wt.% aqueous solution from Sigma was used as such. Solvents of analytical grade such as *N*, *N*-dimethyl formamide (DMF), acetone and glycerol (Shenyang Chemical Reagents)

Plant, China) were used as received. Polyisocyanate (Polymeric form of 4,4'-methylenebis(phenyl isocyanate), Pur system 725A) was purchased from Rohm Haas (Germany) and used as received. Copper chloride (AR, Huzhou Chemical Reagents Plant, China) and deionized water were used for the preparation of copper ion solution.

# 2.2. Preparation of membranes

# 2.2.1. Solution blending of polymers and crosslinking of *PEI*

This study was based on the previous work [30] about the preparation of pure CA membrane and still adopted its optimal composition of casting solution as follows. So the effects of the contents of CA, solvent and glycerol would be discussed no longer. The casting solution of blend polymers of CA/PEI were prepared by blending different compositions of polymers under constant stirring for 4 h at room temperature using a mixture of DMF and acetone (approximate ratio 1.9:1) as solvent. Then, the blended PEI was crosslinked by dropping 7% solution of isocyanate in the same solvent under magnetic stirring. After that, non-solvent additive (glycerol) was added to prepare the casting solution. The content of 50 wt.% PEI in the casting solution was varied from 0 to 2.8 wt.% and the content of CA was approximately 7 wt.%. The mass ratios of solvent and non-solvent additive to CA were maintained at approximate 10:1 and 3.3:1, respectively. The casting solution of pure CA membrane was obtained by absence of PEI and crosslinking agent in above composition of solution.

#### 2.2.2. Membrane preparation

During membrane casting the relative humidity (RH) of room was maintained at 50% and the temperature was kept at 20 °C. The membranes were prepared by employing a two-step process. The membranes with a thickness of 500  $\mu$ m were cast using a casting blade on a glass plate [31] and were allowed to evaporate for 0–30 s. The membranes were kept at the surroundings of 50 °C and RH >95% for 0.5–30 min to induce phase inversion by absorbing water vapor and evaporating acetone, then immersed into distilled water to remove the solvent and additive and solidify the membrane structure. A uniform thickness of 0.18±0.02 mm was maintained for all the membranes in the study.

#### 2.3. Characterization of membranes

All the membranes were characterized in terms of their pure water flux, morphological studies and so on as follows.

#### 2.3.1. Pure water flux (PWF)

The thoroughly washed membranes were loaded in suction microfiltration equipment with efficient filtration area of  $10.3 \text{ cm}^2$ . The flux was measured under steady-state flow with transmembrane pressure kept in 69 kPa (520 mmHg). From the measured values, the PWF was determined from the expression,

$$J_{\rm w} = \frac{Q}{A\Delta T} \tag{1}$$

where  $J_w$  is the water flux (ml/cm<sup>2</sup> min), Q the quantity of water permeated (ml),  $\Delta T$  the sampling time (min) and A the membrane area (cm<sup>2</sup>).

#### 2.3.2. Morphological studies

The top surface and cross-sectional morphology of the membranes were studied using scanning electron microscopy (Hitachi S-3200N, Japan).

# 2.3.3. Porosity

After the membrane was equilibrated in water, the volume occupied by water and the volume of the membrane in the wet state were determined. The membrane porosity was obtained by Eq. (2),

Porosity (%) = 
$$\left[\frac{W_1 - W_2}{d_{\text{water}}}\right] \times \frac{100}{V}$$
 (2)

where  $W_1$  and  $W_2$  stand for the weights of the membranes in the wet and dry states, respectively,  $d_{water}$  the density of pure water at 20 °C, and V the volume of the membrane in the wet state.

#### 2.3.4. Bubble point pressure

Expelling water from a water-wetted membrane by air pressure, water bubble point pressure was measured for estimating the largest pores in a microporous membrane when the first bubble appeared. The largest pore size was determined by the expression,

$$D = \frac{B\gamma\cos\theta}{P} \tag{3}$$

where *P* is the pressure of the first bubble appearing,  $\theta$  the water–solid contact angle between the membrane material and water,  $\gamma$  the water–air surface tension, *D* the pore diameter, and *B* a constant.

#### 2.3.5. Amine end-groups measurement

The ninhydrin method [32] was employed to determine amount of the amine end-groups in resulting membranes, which was about one-fourth of total nitrogen atom in PEI without crosslinking and can show the content of PEI in membranes ignoring the crosslinked proportion of PEI.

#### 2.3.6. BET measurements

The specific adsorption areas of the membranes were determined by  $N_2$ -sorption employing the BET method and using a Micromeritics ASAP 2000 instrument.

# 2.3.7. Adsorption of metal ion

Aqueous solutions of Cu(II) with concentrations varied from 10 to 500 ppm were prepared. The pH values of these solutions were adjusted to 5.0 by adding a small amount of either 0.1 M HCl or 0.1 M NaOH. The pH values in the solutions were measured with Elico pH meter. The static adsorption of Cu<sup>2+</sup> on blend membranes was carried out by a batchwise method. The membranes (15 mg) were shaken in 5 ml of  $Cu^{2+}$  solutions for 2 h [23] at 15 °C. The concentrations of copper ion before and after adsorption were measured by JASCO-v550 UV-Vis (Japan) spectrophotometer at 560 nm, using 0.024% solution of 2-[(5-bromo-2-pyridyl)-azo]-5-diethyl aminophenol (5-Br-PADAP, Beijing Hongyu Chemical Engineering Ltd., China) in 95% ethanol aqueous solution as indicator. The amount of Cu<sup>2+</sup> adsorption was calculated from difference between concentrations before and after adsorption. Five sheets of blend membranes (about 17 mg) with diameter of 13 mm were set into a stack and loaded in the automated Econo System (Bio-Rad, USA) to carry out the dynamic adsorption of  $Cu^{2+}$  with a flow rate of 1 ml/min and  $Cu^{2+}$  concentration of 10 mg/l in the feed. The  $Cu^{2+}$ concentrations in permeate were measured every 0.5 min and breakthrough curves were plotted.

The amount of  $Cu^{2+}$  adsorbed onto the blend membrane, q in equilibrium with the  $Cu^{2+}$  concentration of the feed, was calculated as follows:

$$q = \int_{0}^{V_{\rm s}} (C_0 - C) \frac{\mathrm{d}V}{W_{\rm m}} \tag{4}$$

where  $C_0$  and C are the Cu<sup>2+</sup> concentration of the feed and effluent, respectively,  $V_s$  the effluent volume when C reaches  $C_0$ , and  $W_m$  the weight of the blend membrane.

#### 2.3.8. Adsorption of protein

BSA (Tianjin Biochemical Reagents Plant, China) as a model protein was used to investigate the adsorptions of protein on the blend membranes and Cu<sup>2+</sup>-chelated membranes that were shaken in 500 mg/ml Cu<sup>2+</sup> solutions for 24 h at 15 °C, respectively by the batchwise method. Membranes (20 mg) involving the blend membranes and the Cu<sup>2+</sup>-chelated membranes were washed and equilibrated by shaking in 20 mM sodium phosphate buffer, pH 7.4 with 0.15 M NaCl for 2 h. Then, membranes were shaken in 4 ml of BSA solutions for 24 h [33] at 15 °C. The concentrations of BSA in solutions were measured by JASCO-v550 UV-Vis spectrophotometer at 595 nm according to Bradford method [34]. The amount of BSA adsorption was calculated from difference between concentrations before and after adsorption. The adsorption isotherm was plotted as the adsorption capacity versus the equilibrated concentration of BSA in the solution.

# 3. Results and discussion

In this study, the effects on the membrane performance mainly came from the factors including the time of phase separation induced by water vapor, the amount of blended PEI and the amount of crosslinking agent. The roles played

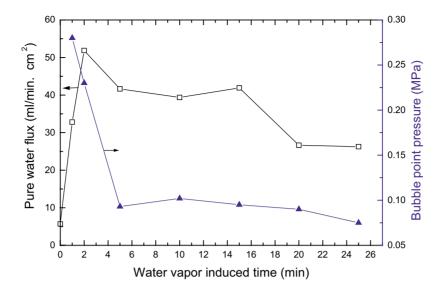


Fig. 1. Pure water flux and bubble point pressure of CA membranes made with different water vapor induced time.

by these factors were investigated and it was attempted to apply the blend membrane to remove heavy metal ion from the aqueous solution and adsorb proteins by ion exchange or affinity interaction with chelated metal ion.

# 3.1. Effects of various factors on the membrane performance

# *3.1.1.* The effect of the time of phase inversion induced by water vapor

Fig. 1 shows the relationship between the membrane performances and the time of phase inversion induced by water vapor. As the induced time increased, the pure water fluxes of the membranes quickly increased and reached the maximum value of  $51.9 \text{ ml/cm}^2$  min at 2 min, then decreased gradually. During this course, the bubble point pressures of the membranes decreased all the while.

According to Mulder [35] and Smolders and coworkers [36], the nucleation and growth of a polymer poor phase is responsible for the pore generation and the cells represent the bulk occupied by the polymer poor phase. Fig. 2 shows the structure of pure CA membranes, which have different time of phase inversion induced by water vapor during the preparation. When a little induced time like 0.5 min was employed, which represented altering immersion precipitation to two-step phase separation process, a complete change in morphology could be observed. As the induced time increased from 0 to 2 min, the structures of membranes changed from an asymmetrical structure with a dense layer and finger-like macrovoids to symmetrical structure with sponge-like pore. With the time further increased, a cellular structure by the coarsening of polymer-lean phase at the late stage of phase separation was formed and solidified at last. The size of cell increased and resulted in enlargement of the pore size with increasing the induced time, but the interconnectivity of cell decreased. So the max PWF in Fig. 1 could represent a compromise between the nucleation and growth of the polymer-lean phase.

The phenomena can be explained as follows. When the membrane is solidified at the stage of nucleation prevailing over growth, the cells have a high interconnectivity. With the growth of polymer poor phase, the size of cell increases, but the interconnectivity of pore is reduced because the growth process thicken polymer rich phase between the cells simultaneously. When the membrane is solidified after complete growth, the cells are blocked out. Obviously, the pore size and permeate performance of membrane depend on the size and density of the interconnected part of the cells. So membrane can have optimal permeate performance at the transition stage of the two cases.

When the 2 min-induced time was adopted, the pure CA membrane would strongly wrinkle because of inhomogeneous inner stress during the second step process of immersion into water. This tendency of membranes to wrinkle can be effectively restrained with increasing amounts of PEI in casting solutions beyond a mass ratio of 50% PEI and CA, 1:10. The membranes, prepared by adopting the 2 min-induced time in this study, have good breaking resistance while being folded. So the water vapor induced time of 2 min was appropriate during the preparation of blend membranes.

#### 3.1.2. The effects of the amounts of PEI in casting solutions

The effects of amount of PEI in casting solutions on membrane performance are shown in Figs. 3–5. It is evident from the figures that an increase in PEI content decreases pore size, interconnectivity of pore and PWF of membranes. When the mass ratio of 50% PEI and CA is more than 0.15, the PWF is approximately equal to zero, which means that the interconnectivity of pore is completely destroyed from the analysis of Figs. 4 and 5. When a little amount of PEI was blended and easy to be dissolved in water, the lost PEI played a role in the formation of membrane pore as a porogen. Thus, it was explained that the PWF of membranes first increased and then decreased with increasing blended amount of PEI as shown in Fig. 3. Fig. 3 also shows an increase in amount of amine groups in membranes with increasing amounts of PEI in casting solutions. But the calculation shows based on the amount of amine groups that there is more than 80% of blended PEI

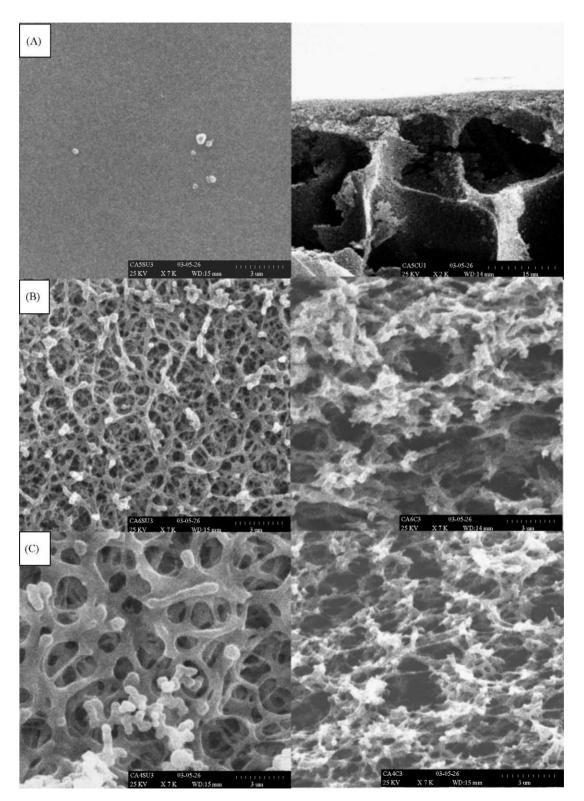


Fig. 2. SEM images of the air surfaces (left) and the cross-sections (right) of the membranes made of CA with different time of phase inversion by water vapor: (A) 0 min (immersion precipitation); (B) 0.5 min; (C) 1 min; (D) 2 min; (E) 4 min; (F) 8 min.

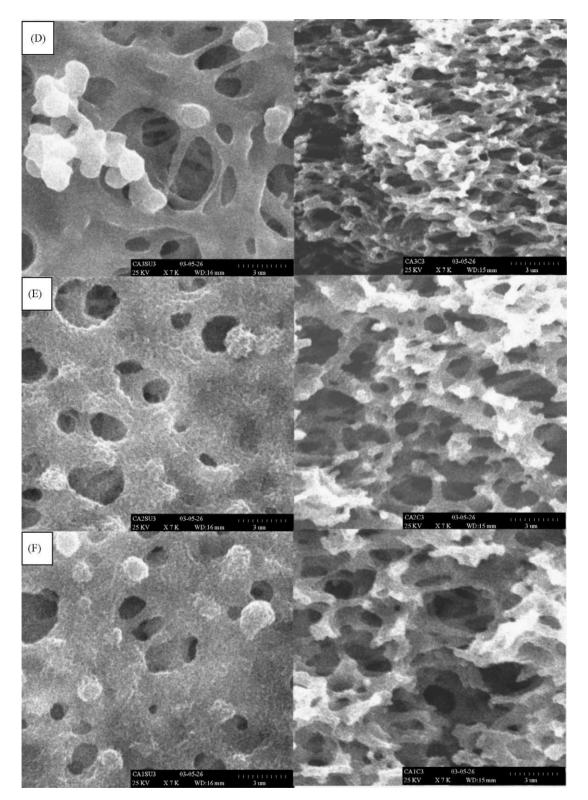


Fig. 2. (Continued).

lost during preparation and washing of blend membranes. So the stable presence of PEI in membranes cannot be achieved by simply blending because of the solubility of PEI in water.

# 3.1.3. The effects of the amount of crosslinking agent

In this study, the effects of crosslinking on membrane performance are complex and various. The amine groups of blended PEI can slowly react with acetone in solution to

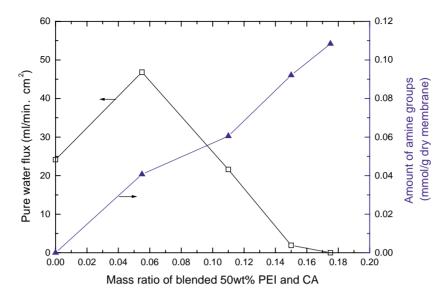


Fig. 3. Pure water flux and amount of amine groups of blend membranes made of different mass ratio of 50 wt.% PEI and CA in the casting solution. The water vapor induced time is 2 min.

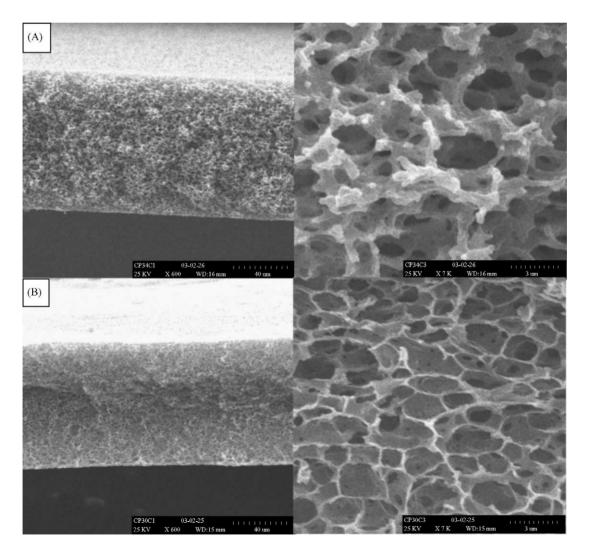


Fig. 4. SEM images of the cross-sections (left) and its magnification (right) of the blend membranes made of different mass ratios of 50% PEI and CA in casting solutions: (A) 0.05; (B) 0.175. The water vapor induced time is 6 min.

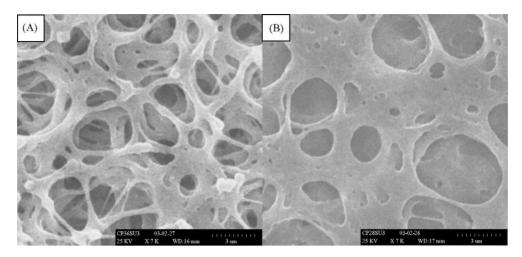


Fig. 5. SEM images of the air surfaces of the blend membranes made of different mass ratios of 50% PEI and CA in casting solutions: (A) 0.1; (B) 0.175. The water vapor induced time is 2 min.

form schiff base with color changed. Therefore, there exists a moderate time interval about 20 h between blending of PEI into CA solution and crosslinking of PEI so that PEI can be sufficiently dispersed and insoluble tendency of crosslinked PEI can be kept at the minimum level. There was a limitation in the 50% PEI/CA ratio about 0.17, above which the products of crosslinking reaction contained a lot of insoluble deposit After being crosslinked at a moderate degree, an opaque polymer solution without insoluble deposit and aggregation was obtained, into which glycerol was added to prepare a casting solution.

Fig. 6 shows the effects of amount of crosslinking agent on PWF and amount of amine groups of membranes made of a 0.15 PEI/CA ratio. The increasing tendency on amine groups was observed with increasing crosslinking agent/PEI ratio. The crosslinking makes more PEI present in resulting membranes and enhanced the stability of membrane performance. As the ratio is close to 1, the change rate of amine groups was slowed down. That indicates that the role of crosslinking agent has been brought into play sufficiently and further increasing in crosslinking agent will lead to overcrosslinking. With increasing crosslinking agent/PEI ratio, the PWF increased at first and decreased after it reached the maximum value of 37.0 ml/cm<sup>2</sup> min near the ratio of 0.5.

The SEM images of air surfaces and cross-sections of the membranes with different crosslinking agent/PEI ratio are shown in Fig. 7. With increasing crosslinking agent/PEI ratio from 0 to 1, the pore interconnectivity is enhanced and the pore size of the blend membrane diminishes gradually. That can explain the change tendency of PWF with changing crosslinking agent/PEI ratio shown in Fig. 6.

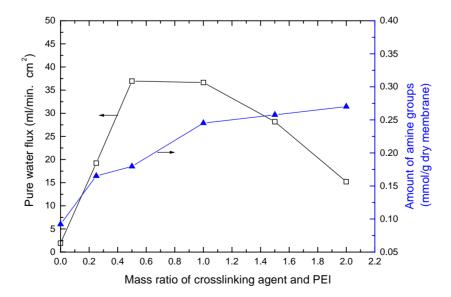


Fig. 6. Pure water flux and amount of amine groups of membranes made of different mass ratio of crosslinking agent and PEI and a 0.15 mass ratio of blended 50 wt.% PEI and CA. The water vapor induced time is 2 min.

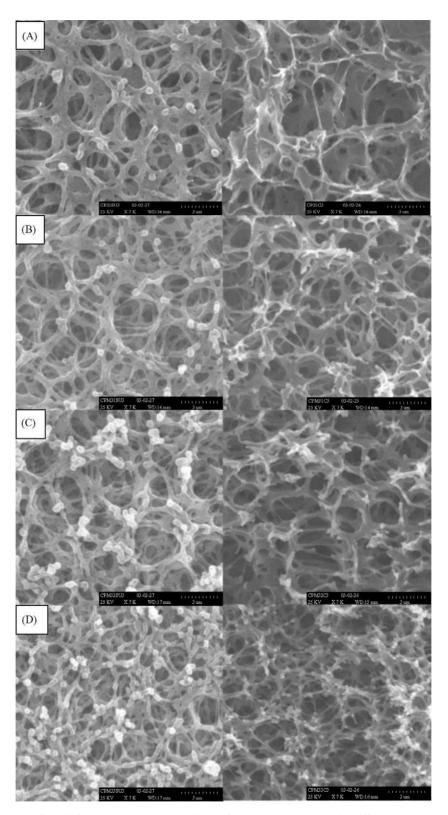


Fig. 7. SEM images of the air surfaces (left) and the cross-sections (right) of the blend membranes with different mass ratios of crosslinking agent and PEI in casting solution: (A) 0; (B) 0.25; (C) 0.5; (D) 1. The mass ratios of 50% PEI and CA in casting solutions and the water vapor induced time were 0.15 and 2 min, respectively.

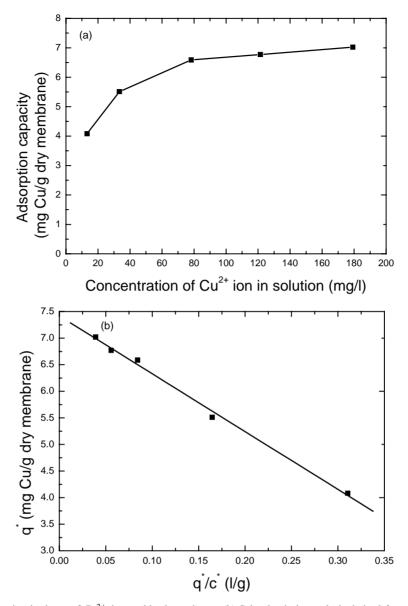


Fig. 8. (a) Adsorption isotherm of  $Cu^{2+}$  ion on blend membrane; (b) Schatchard plot analysis derived from adsorption data.

Through choosing appropriate amounts of PEI and crosslinking agent, we can prepare blend membranes which have specific surface area of  $12.04-24.11 \text{ m}^2/\text{g}$ , as determined by N<sub>2</sub> adsorption and PWF of  $10-50 \text{ ml/cm}^2 \text{ min}$  with porosity of 63-75%.

The investigations in applications of the membrane, made of 0.15 50 wt.% PEI/CA ratio and 0.5 crosslinking agent/PEI ratio, are shown as follows.

#### 3.2. Adsorption of Cu(II) ion onto the blend membranes

#### 3.2.1. Static adsorption of Cu(II) ion

The equilibrium data for adsorption Cu(II) on the blend membrane at pH 5.0 are plotted in Fig. 8. The Langmuir isotherm equation provided excellent fit to the equilibrium adsorption data, giving a correlation coefficient,  $r^2 = 0.996$ . The Langmuir isotherm is written as follows:

$$q^* = \frac{q_{\rm m}c^*}{c^* + K_{\rm d}}\tag{5}$$

where  $q^*$  is the equilibrium adsorption amount (mg Cu/g dry membrane),  $c^*$  the equilibrium concentration of Cu(II) (mg/l), and the parameters  $q_m$  and  $K_d$  represent the maximum adsorption capacity and the dissociation constant, respectively. The data were fitted to the single-solute Langmuir isotherm equation by Schatchard plot and the parameters  $q_m$  and  $K_d$  are 7.42 mg/g membrane and  $1.71 \times 10^{-4}$  mol/l, respectively. The maximum capacity of the blend membrane is about 40% of the result of Duru et al. [23]. In order to remove heavy metal ion from aquatic system efficiently, it is necessary to improve the content of PEI in resulting membranes. However, the improved density of ligand will

Table 1 Reuse of membranes for  $Cu^{2+}$  ion adsorption

	Reuse times		
	1	2	3
Adsorption amount (mg/g)	7.62	5.52	5.25

result in a relatively low PWF of membrane. So further optimization for the preparation of blend membranes is also necessary.

The membranes (15 mg) were shaken in 5 ml of 150 mg/l  $Cu^{2+}$  solutions for 2 h [23] at 15 °C. After balance of adsorption was reached, the membranes were washed completely with deion water and then were eluted with 4 ml 0.1N hydrochloric acid. The adsorption amount was determined by measuring concentration of elution solution. At last, the membranes were dipped into deion water and washed completely so as to reuse. A circle every 2 weeks, the reuse of the membranes was investigation and the results were shown in Table 1. There is about 30% reduction between adsorption amounts of first time and second time. Then, the difference between second and third time was kept at a low level. The results indicated that adsorption amount of  $Cu^{2+}$  ion on membrane reached a stable value after the components prone to depart was washed.

# 3.2.2. Breakthrough curve of the membrane absorbers

The Cu<sup>2+</sup> solutions about 10 mg/l were permeated through the different types of PEI/CA blend membranes at a flow-rate of 1 ml/min. The breakthrough curve was obtained by plotting the concentration of Cu<sup>2+</sup> in permeate against the volume of permeate in Fig. 9. The adsorption capacity calculated according to Eq. (4) is about 3.3 mg/g, which is consistent with the value 3.55 mg/g, calculated from Langmuir model with equilibrated  $Cu^{2+}$  concentration, 10 mg/l. The results show that by using the blend membrane, low concentration  $Cu^{2+}$  ion can be removed from wastewater conveniently.

# 3.3. Adsorption isotherms of protein onto the membranes

In a batch system, BSA as a model protein was used to investigate the adsorptions of protein on pure CA membranes and the blend membranes with and without chelating Cu<sup>2+</sup>, respectively. The adsorption isotherms of BSA on the membranes were measured and plotted in Fig. 10. Curve 3 in Fig. 10(a) shows the adsorption of BSA on pure CA membranes is at a very low level which means that non-selective protein binding of the membranes can be kept at a low level. The bound protein concentration based on membrane weight  $(q^*)$  was plotted against the free protein concentration  $(c^*)$  in solution at equilibrium. To determine the dissociation equilibrium constant  $(K_d)$  and maximum binding capacity  $(q_m)$ , these data were fitted to the single-solute Langmuir isotherm equation as described above.

The fitted values were shown in Table 2, among which the molecular weight of BSA is taken as 66 700. There is about two times difference between the maximum adsorption capacities of BSA on the membranes with and without chelating  $Cu^{2+}$  ion. The differences from the equilibrium adsorption parameters,  $q_m$  and  $K_d$ , show that there are two interactions, chelating metal ion affinity and ion exchange, between BSA and membranes with and without chelating  $Cu^{2+}$  ion, respectively. Iwata et al. [33] have reported that the IDA-Cu ligand-containing adsorbent based on grafted polyethylene hollow fiber had a binding capacity for BSA of 42 mg/g which was about half of the result of PEI-Cu ligand-containing membrane in this work. Although seldom

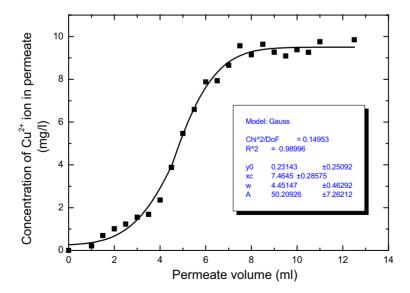


Fig. 9. Breakthrough curve for  $Cu^{2+}$  ion at 1 ml/min. The membrane was made of a 0.15 mass ratio of blended 50 wt.% PEI and CA and a 0.5 ratio of crosslinking agent and PEI.

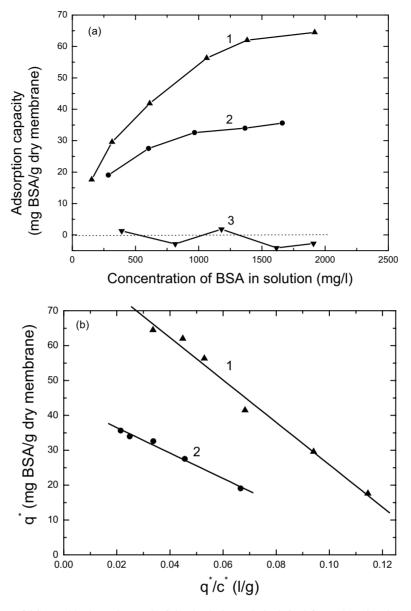


Fig. 10. (a) Adsorption isotherm of BSA on blend membrane; (b) Schatchard plot analysis derived from adsorption data. The curves 1 and 2 represent the membranes with and without chelating  $Cu^{2+}$  ion, respectively. The curve 3 represents CA membranes.

Table 2 The equilibrium adsorption parameters of  $\mathrm{Cu}^{2+}$  ion and BSA on the membranes

Parameters	Adsorption of Cu <sup>2+</sup> ion	Adsorption of BSA on membranes		
		Without Cu <sup>2+</sup> ion	With Cu <sup>2+</sup> ion chelated	
$\overline{K_{\rm d}} \ ({\rm mol/l})$	$1.71 \times 10^{-4}$	$5.46 \times 10^{-6}$	$9.11 \times 10^{-6}$	
$q_{\rm m}$ (mg/g dry membrane)	7.42	43.8	86.6	
$q_{\rm m}$ (mg/g dry membrane) $R^2$	0.996	0.988	0.985	
Std.	0.0917	0.8678	2.596	

mentioned or discussed, it is obviously possible to use PEI as metal chelator instead of iminodiacetic acid. So we provide an alternative method for preparation of immobilized metal ion affinity membrane here.

# 4. Conclusion

In this work, cellulose acetate as a matrix polymer was blended with polyethyleneimine in a mixture of solvents to prepare a modified microfiltration membrane. PEI was blended into CA solution and subsequently crosslinked with isocyanate for stable presence of PEI in the resulting membranes and improved membrane performance. Through investigating the effects of various factors and optimizing the conditions of preparing membrane, we can prepare the basic membranes with homogeneously microporous structure, large internal surface area, high pore interconnectivity and mechanical stability. The membrane is suitable for separating biomolecules, complexing heavy metal or further coupling ligand.

This work employed the Langmuir model to determine the sorption equilibrium and rate constants. The maximum adsorption capacity of  $Cu^{2+}$  ion on the blend membrane is 0.117 mmol/g dry membrane. The maximum adsorption capacities of BSA on the membranes with and without chelating  $Cu^{2+}$  ion are 86.6 and 43.8 mg/g dry membrane, respectively. The differences from the equilibrium adsorption parameters of BSA on membranes show that there are two interactions, chelating metal ion affinity and ion exchange, between BSA and membranes with and without chelating  $Cu^{2+}$  ion, respectively. Thus, we can provide an alternative method by using PEI as metal chelator instead of iminodiacetic acid for preparation of immobilized metal ion affinity membrane.

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