

Preparation, Characterization, and Testing of a Composite Membrane with pH Sensitivity

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ABSTRACT: In this article, a novel poly-(acrylic acid-acrylonitrile) (PAA-AN)/filter paper composite membrane with pH-sensitivity was developed. The membrane was composed of three layers. The top and bottom layers were made of PAA-AN copolymer, while the middle layer was filter paper. The filter paper was used to enhance the strength of the membrane. The PAA-AN/filter paper membrane showed evident pH sensitivity and pH reversibility as the pH value changed between 2.0 and 9.5. With

the increase of the PAA-AN copolymer amount in the composite membrane, the pH sensitivity increased. The Cu (II) ion-exchange experiment indicated that the membrane could bind metal ions and could be used as ion-exchange membrane to purify water. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 3607–3614, 2011

Key words: poly-(acrylic acid- acrylonitrile); filter paper; membrane; pH-sensitive

INTRODUCTION

The pH-sensitivity as a novel and powerful technique has been widely used in the biotechnology industry for drug delivery systems and advanced separation. Compared with thermosensitive, it gives more choices both for the materials and applying environment. pH-sensitive hydrogels^{1–3} and polymer interpenetrating networks microspheres^{4–7} have been intensively investigated. With respect to pH-sensitive membranes, Childs and coworkers⁸ provided a new type of membrane composed of a microfiltration substrate and a pore-filling polyelectrolyte produced by UV induced grafting of 4-vinylpyridine onto polyethylene and polypropylene microfiltration membranes. The membranes showed an outstanding pH valve effect and the capability of rejecting small inorganic ions in the process of reverse osmosis. Thereafter, the effect of the cross-linking of the polyelectrolyte on the flux and separation, the effect of

polyelectrolyte composition on the membrane performance, and the effect of gel layer thickness on the salt rejection performance were investigated.^{9–12} Lee et al¹³ produced a new type of membrane by both plasma induced grafting and UV induced grafting of acrylic monomers on the surface of commercial polyamide membranes. These membranes showed outstanding pH-valve effect and the capability of drug permeation. Hu and Dickson¹⁴ developed a pore-filled pH-sensitive membrane by in situ cross-linking poly (acrylic acid) (PAA) inside poly (vinylidene fluoride) hydrophobic microporous substrate membranes, and the membranes demonstrated a rapid and reversible response of flux to environmental pH as the pH was changed between 2.5 and 7.4. Lai et al¹⁵ reported an efficient method for fabricating pH-sensitive membranes. To obtain these membranes by phase inversion methods, poly(ethylene-co-vinyl-alcohol) and PAA were separately dissolved in water and ethanol, respectively. And then the two solutions were mixed in desired proportions. However, only a small amount of PAA retained in the membranes. To increase the PAA amount in the membrane, PAA submicrogels were synthesized to blend into polyethersulfone membranes in our earlier study.¹⁶

poly-(acrylic acid-acrylonitrile) (PAA-AN) copolymer is one kind of materials with pH-sensitivity and much attention has been taken to the study of it. Kobayashi et al^{17–20} prepared molecular imprinting membranes of theophylline by phase inversion with PAA-AN. In another study,²¹ membranes, based on a PAA-AN copolymer, produced through phase

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inversion, were modified by introducing specific binding sites for uric acid into their structure. Nanoporous molecularly imprinting copolymer PAA-AN membrane (DICMI) could be synthesized by wet phase inversion method, using D-Phenylalanine as the template, for the optical resolution of amino acid. And the membrane was intended for the selective separation of phenylalanine.²² Sahoo et al²³ synthesized PAA-AN block copolymer by controlled dosing method of free radical polymerization. The polymer was converted into fibers by wet solution spinning technique in DMF-water system, and the resulting fibers showed pH sensitivity. Moreover, many other studies^{24–27} focused on the preparation and separation performance of PAA-AN copolymer membranes. The goal of this study is to prepare pH-sensitive membrane by directly coating PAA-AN copolymer onto filter paper, and obtain a composite membrane with high carboxyl groups.

Filter paper is a kind of good basis material and widely used in chromatography fields. Yang et al^{28,29} produced several kinds of chitosan/filter paper composite membrane for chromatography. These membranes showed both high proteoexy and dynamic binding capacity of human IgG. In another study, Cifci and Polat³⁰ reported an efficient method for fabricating ion-exchange membrane by coating poly(vinyl alcohol)-alginate mixture solutions on the filter paper.

In this study, we provided an easy and economical method to prepare pH-sensitive and ion-exchange membranes by coating PAA-AN on both sides of filter papers. The PAA-AN copolymer was synthesized in *N*-methyl-2-pyrrolidone (NMP) solution by free radical polymerization. By using a phase inversion method, the PAA-AN/filter paper composite membranes were prepared. In this case, the PAA-AN layers were coated on both surfaces of the filter paper. The filter paper was used to enhance the strength of the membrane. The pH-valve effect on the membranes, the ion-exchange capacity (IEC) and the copper adsorption were also investigated.

EXPERIMENTAL

Materials

Acrylonitrile (AN; AR, 98.0%) was purchased from UNI-CHEM (Tianjin, China). Acrylic acid (AA; AR) was purchased from Chengdu Kelong Chemical Reagent Company (Chengdu, China). Both AN and AA were pretreated by activated carbons before use. *N*-methyl-2-pyrrolidone (NMP; AR, 99.0%) was purchased from Chengdu Kelong (Chengdu, China), and used as the solvent. Azo-bis-isobutyronitrile (AIBN) was purchased from Shishihwei Chemical Reagent (Shanghai, China), and used as the initiator. All the other chemicals (analytical grade) and mate-

TABLE I
Details of the High, Medium, and Low Speed Filter Papers

	Pore size (μm)	Particle retention data (μm)	Grade
High speed filter paper	20	15	101
Medium speed filter paper	10–15	10	102
Low speed filter paper	5–10	5	103

rials were obtained from the Chengdu Kelong (Chengdu, China), and were used without further purification. Filter paper was purchased from Hangzhou Special Paper Industry Company (Hangzhou, China). The details of the high, medium, and low speed filter papers are shown in Table I.

Synthesis of poly(acrylonitrile-co-acrylic acid)

AN and AA (mol ratio 2 : 1) were dissolved in NMP with the monomer concentration of 30 wt %. The initiator, AIBN was introduced into the mixture solution at 0.3 wt % of the total monomer weight, and then the solution was stirred vigorously until all the monomers were completely dissolved. Polymerization was carried out in a three-necked bottle at 65°C for 24 h. Then the production was washed several times with double distilled water and ethanol respectively to remove the residual monomers, some homopolymers, and the solvent thoroughly, which were confirmed by UV scanning. The obtained copolymer was dried at 60°C in a vacuum oven for over 72 h.

Characterization of poly(acrylonitrile-co-acrylic acid)

To prepare Fourier transform infrared spectroscopy (FTIR), the copolymer was dissolved in tetrahydrofuran, and cast on a potassium bromide (KBr) disc with the thickness of about 0.8 mm, and then the cast polymer solution was dried by an infrared light to remove the tetrahydrofuran NMP. The FTIR spectra were measured with FTIR Nicolet 560 (Madison, Wisconsin).

Elemental analysis, which is based on the determination of hydrogen (H) and nitrogen (N),^{31–33} was performed using a CARLO ERBA 1106 elemental analyzer (Italy), with a carrier gas (He, at a flow rate of 100 mL/min) at a combustion temperature of 1000°C. The inverse proportions of C, H and N were determined. Thus, the chain proportions of AN and AA could be obtained.

GPC measurement, which is based on the liquid chromatography analysis using an aqueous gel permeation column, was performed by using a PL220

GPC analyzer (Britain), and *N, N*-dimethyl formamide (DMF) was chosen as the eluent.

Membrane preparation

Membranes used in this study were prepared by liquid-liquid phase inversion technique.^{34–36} Since the composite membrane was applied in aqueous medium, both sides of the filter paper were coated with the copolymer of PAA-AN. The copolymer was dissolved into NMP to obtain the casting solution. The concentration of the copolymer was 22, 20, and 18%, respectively (The optimum concentration of the casting solution is about 20%. It is difficult to prepare membrane when the concentration of the casting solution is over 25% or below 15%). In the experiments, different membranes were prepared by changing the spin coating speed. Briefly, after vacuum degassed, the casting solution was first coated on one side of the filter paper by spin coating coupled with a liquid-liquid phase separation technique at room temperature. Then the composite membranes were dried at 50°C in an oven for 2 h. After the membranes were completely dried, the casting solution was then coated on the other side of the filter paper by the same method which mentioned above. The membranes were rinsed with distilled water thoroughly to remove the residual solvent. The composition of the membranes is shown in Table II.

Scanning electron microscope (SEM) of the membrane

For the SEM observation, the membrane samples were freeze-dried at their acidic form, and then quenched by liquid nitrogenous gas, attached to the sample supports and coated with a gold layer. A SEM (JSM-5900LV, JEOL, Japan) was used for the morphology observation of the membrane cross section.

Determination of IEC

To measure the IEC, a membrane sample was alternately equilibrated by 0.1M HCl and 0.1M NaOH solutions for a couple of times, and washed by double distilled water in between. Afterwards, a piece of dried membrane with certain weight was immersed into 0.1M NaOH solution and stirred for 24 h. Then the solution was titrated with 0.1M HCl solution. The IEC was calculated by eq (1):

$$\text{IEC}(\text{mequiv/g}) = \frac{V_{\text{HCl}}N_{\text{HCl}} - V_{\text{NaOH}}N_{\text{NaOH}}}{m_c} \times 1000 \quad (1)$$

where V_{HCl} (L) and V_{NaOH} (L) are the volumes of the HCl and NaOH solutions, respectively. N_{HCl}

TABLE II
The Compositions of the PAA-AN/Filter Paper Composite Membranes

Membrane No.	The concentration of the copolymer solution (wt %)	The spin coating speed of the membrane (rpm)	The thickness membranes (μm)
M-20-1000	20	1000	200
M-20-800	20	800	240
M-20-600	20	600	300
M-18-300	18	300	300
M-22-400	22	400	300

(mol/L) and N_{NaOH} (mol/L) are the normalities of the HCl and NaOH solutions, respectively. m_c (g) is the weight of the dried membrane.

Permeation experiments

The membrane water flux as a function of pH was investigated by using an apparatus as described in previous studies.^{35,37} The pressure was supplied by an air compressor. The dead-end ultrafiltration (UF) cell was used with an effective membrane area of 13.8 cm². The test membranes were precompact at 0.05 MPa by pH 2.2 solution flow for 30 min to get steady filtration. Then, the water flux was determined at the pH values ranging from 2.2 to 9.5, randomly. The water flux was expressed as the hydrodynamic permeability, and calculated by eq. (2):

$$\text{Flux}[\text{mL}/(\text{m}^2 \text{h mmHg})] = \frac{V}{S \times t \times P} \quad (2)$$

where V was the volume of the permeated solution, mL; S the effective membrane area, m²; t the time of the solution collecting, h; P the pressure on the membrane, mmHg.

The membrane solution flux response to pH changing was also carried out. The test membranes were precompact at 0.08 MPa for 30 min by pH 2.4 buffer solution flow. Then, the cell was alternatively fed by pH 8.5 NaOH and pH 2.4 HCl solutions at 0.05 MPa with a short double distilled water cleaning in between by opening the cell and washing the membrane. The permeated solution was collected over 4 min and after 4 min equilibration by the feed flow. All the flux measurements were conducted at room temperature.

Adsorption of Cu (II)

To investigate the adsorption capability of the heavy metal, Cu (II) ion was used as a model metal ion. Cu (II) ion could be found in effluents and was known to cause liver cirrhosis and to decrease

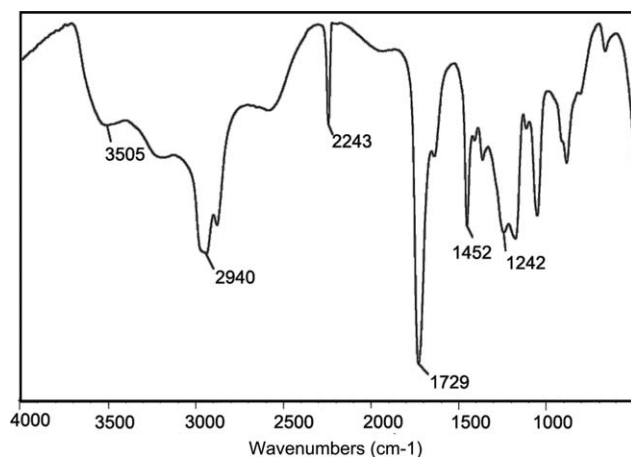


Figure 1 FTIR spectra of PAA-AN copolymer.

photosynthesis.^{38,39} The feasibility of the UF process in copper ion removal was demonstrated for the membrane (M-22-400) using the apparatus described above. To test the adsorption ratio of Cu (II), 10 mL of 1 mmol/L, 10 mmol/L, and 100 mmol/L CuSO₄ solutions were applied to the membrane at the pressure of 0.05 MPa, respectively. The concentration of Cu (II) was determined by an atomic adsorption spectrophotometer (Shimadzu SPCA-626D, Japan). The adsorption quantity of Cu (II) (mmol) was calculated by eq (3):

$$N = (C_0 - C_1) \times 0.01 \quad (3)$$

where N (mmol) is the adsorption quantity of Cu (II) (mmol). C_1 (mmol/L) and C_0 (mmol/L) are the normalities of the CuSO₄ solutions that used before and after the adsorption.

RESULT AND DISCUSSION

FTIR analysis

Figure 1 shows the FTIR spectra of the copolymer PAA-AN. It can be seen that the peaks at 3505, 1729, and 1242 cm⁻¹ were the characteristic peaks of the -OH, C=O and -C-O- in the carboxyl group of AA, respectively. The peak at 2243 cm⁻¹ could attribute to the -CN of the AN chains in the copolymer. Furthermore, the peaks at 2940 cm⁻¹ and 1452 cm⁻¹ attribute to the -CH₂- and -CH- in the trunk chain of the copolymer, respectively. The FTIR spectra indicated that the copolymer of PAA-AN was synthesized.

Elemental analysis and GPC measurement

The proportions of nitrogen and hydrogen in the copolymer were 14.03 and 6.10%, respectively. Then the chain proportions of AN and AA were calcu-

lated as 57.1 and 42.9%, respectively. Compared with the monomers used in the polymerization (the monomers proportions of AN and AA were 66.7 and 33.3%, respectively), the AA content became larger in the copolymer chain. This might be explained by the reactivity ratios of AA and AN, which are 2.45 and 0.53, respectively.⁴⁰ The values of $r_{AN} < 1$ and $r_{AA} > 1$ indicated that the propagation reaction $\sim\sim\sim AA-AA^\circ$ and $\sim\sim\sim AN-AA^\circ$ will be preferred over $\sim\sim\sim AA-AN^\circ$ and $\sim\sim\sim AN-AN^\circ$. Hence, the probability of AA units entered into the copolymer chains was higher than that of AN units.⁴¹ Furthermore, the molecular weight obtained by GPC for PANAA was $M_n = 52,000$, and the dispersity was 5.528.

Morphology of the composite membrane

SEM pictures of the cross section views of the membranes are shown in Figure 2. As shown in the figure, a trilayer-structure was obviously observed. The top and the bottom of the composite membrane were the PAA-AN copolymer (a), while the middle of the composite membrane was the filter paper (b). It can also be found that the three layers combined well from the SEM. The copolymer could enter into the pores of the filter paper, and adhered onto the filter paper very well.

The purpose of using filter paper in the study is to increase the strength of PAA-AN/filter paper composite membrane. We used high-speed filter paper, medium-speed filter paper, and low-speed filter paper in the study. The results indicated that there was no significant difference between the composite membranes with different types of the filter papers. The tensile strength and tensile elasticity modulus of composite membrane are shown in Table III. As shown in the table, the composite membranes with copolymer on both sides had the highest mechanical

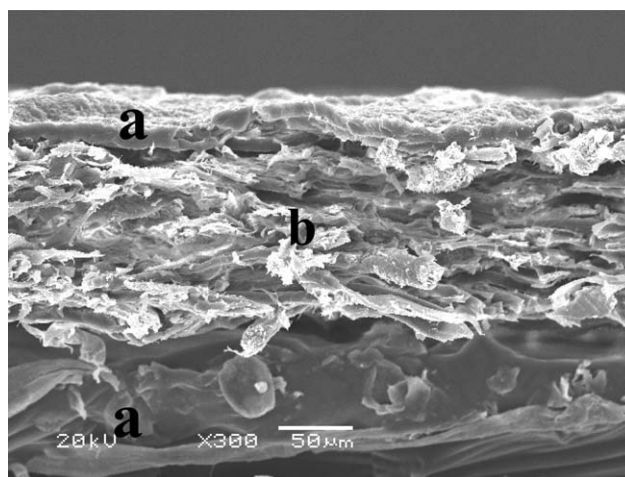


Figure 2 SEM image of the cross section view of the PAA-AN/filter paper composite membrane.

TABLE III
The Mechanical Properties of the PAA-AN/Filter Paper Composite Membranes

Sample	Tensile elasticity modulus (MPa)	Tensile strength (MPa)
Filter paper	1802.04	14.99
Composite membrane with copolymer on one side	1882.8	26.60
Composite membranes with copolymer on both sides	2023.5	39.25

Duplicate experiments showed similar results.

properties, and tensile strength and tensile elasticity modulus of composite membrane were 39.25 and 2023.5 MPa, respectively. In addition, the PAA-AN copolymer membrane without the filter paper had weak strength, and could not be used as UF membrane, especially at high pressure.

Ion-exchange capacity

The charge property of the composite membranes was investigated in terms of membrane IEC. The IECs obtained by titration are given in Table IV. As shown in the table, the IECs of the membrane were between 1 to 2.5 mequiv/g, which were similar to those of the reported commercial ion-exchange membranes (1–2 mequiv/g).⁴²

Compared with the IECs of the membranes (M-20-1000, M-20-800, and M-20-600), it can be seen that the IECs of the membranes increased with the increase of the membrane thickness due to the large amounts of the coated copolymers. For the membranes with the same thickness, the IECs of the membranes increased with the increase of the PAA-AN concentration in the casting solution, since the mass fraction of the PAA-AN copolymer in the composite membrane increased.

Membrane water flux as a function of pH value

The effect of pH changing from 2 to 10.5 on water flux through three membranes (M-20-1000, M-20-

TABLE IV
The Titrated IECs of the PAA-AN/Filter Paper Composite Membranes

Membrane No.	Titrated IECs for the membranes (mequiv/g)
M-20-1000	0.9566
M-20-800	1.3025
M-20-600	1.8187
M-18-300	1.2046
M-22-400	2.5274

Duplicate experiments showed similar results.

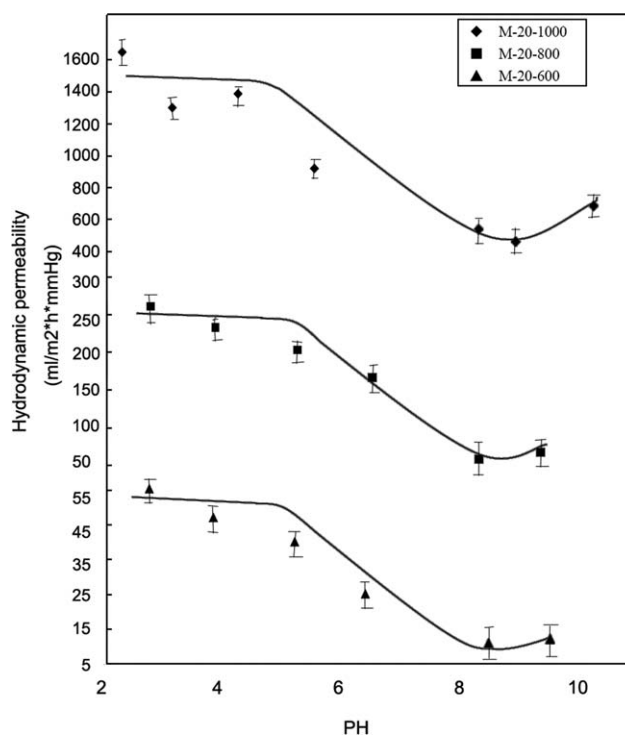


Figure 3 Water flux as a function of pH for the membranes M-20-1000 (◆, the spin coating speed was 1000 rpm); M-20-800 (■, the spin coating speed was 800 rpm); M-20-600 (▲, the spin coating speed was 600 rpm). Duplicate experiments showed similar results.

800, and M-20-600), with the same concentration of the copolymer in the casting solution but different spin coating speed, was studied and the results are presented in Figure 3. As shown in the figure, when the spin coating speed increased, the water flux increased due to the smaller thickness as shown in Table I; while the flux change was smaller due to the smaller amount of the copolymer in the composite membrane.

The water fluxes of the membranes exhibited chemical valve behavior at pH between 3 and 9, and hardly changed at the pH value lowered than 3. For M-20-1000, a flux variation of two numerical values was observed, from 1648.6 mL/(h m² mmHg) at pH 2.3 to 467.4 mL/(h m² mmHg) at pH 9.1; and that changed from 55.6 to 11.1 mL/(h m² mmHg) for M-20-600. The chain configuration of weak polyacid is a function of pKa of the polymer. The pKa of PAA-AN in solution is about 4.3–4.9,^{43,44} dependent upon the measurement method, which is in agreement with that from Figure 2. Thus, at pH values lower than 3, at least 90% of the carboxyl groups were in their unionized state. The PAA-AN chains coiled down resulting in pore increasing. At pH values higher than 7, about 85% of the carboxyl groups dissociated and extended resulting in pore decreasing.¹⁶

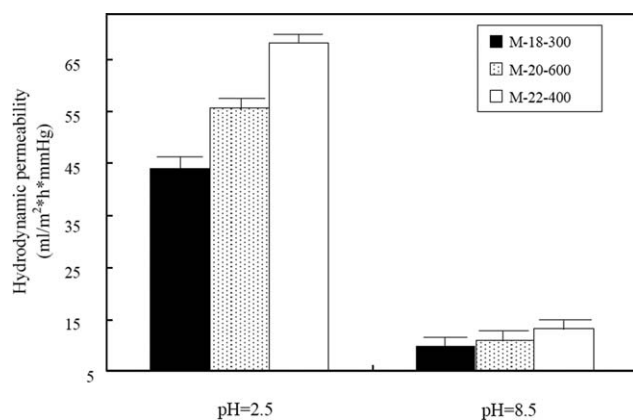


Figure 4 Water flux as a function of the PAA-AN concentration of the casting solution in membrane preparation. Duplicate experiments showed similar results.

When the pH value was larger than 9, the flux did not decrease, but increased. This result may seem counterintuitive because the chain volume would be expected to swell right along. This was caused by the decreasing in the volume charge density of the ionic groups. The mobility of chains surrounded by a polyelectrolyte layer is an increasing function of the volume charge density of the ionic groups. This effect, combined with the appreciable ionic strength due to the added base, appears to overwhelm the expected total increase in net charge.

The water flux for the membranes at pH over 11 could not be obtained. At very high pH, the carboxyl groups in the copolymer and cellulose could react with NaOH, the composite membrane was destroyed and could not be used.

Effect of the concentration of the casting solution on water flux

The water fluxes for three sample membranes (M-20-600, M-22-400, and M-18-300) with the same thickness and different concentrations of copolymer in casting solutions were studied and the results are presented in Figure 4. As shown in the figure, with the increase of the copolymer concentration in the casting solutions, the flux increased both under acid and normal conditions. It is known that the flux was affected by the pore size of the membrane (membrane structure) and the hydrophilic of the membrane. At higher concentration, the membrane structure will be dense, however, the content of the copolymer increased, and the content of acrylic acid increased. Thus, the hydrophilicity of the composite membrane increased. As a result, the flux increased with the increase in concentration of the casting solution in this study.

As shown in Figure 3, with the increase of the spinning speed, the water flux increased, since the

membrane thickness decreased. With the increase of the copolymer concentration in the casting solution, the flux also increased as shown in Figure 4. Moreover, when the thickness of the membrane is too small, the membrane cannot be used. Thus, the optimum thickness of the membrane is between 100 and 400 μm , the spinning speed was 600 rpm, and the casting concentration was 20%. The water flux for the optimum membrane ranged from 11 to 56 $\text{mL}/(\text{h m}^2 \text{ mmHg})$, which were similar to those of the reported membranes.^{45,46}

Membrane pH reversibility

To study the membrane flux as a function of environmental pH, the pH reversibility of the membrane M-20-800 was evaluated by the solution flux at the pH 2.4 or 8.5, data are shown in Figure 5. As shown in the figure, the hydrodynamic permeability was reversible between 230 and 70 $\text{mL}/(\text{h m}^2 \text{ mmHg})$ as the solution was alternated.

The PAA-AN layers were coated on both sides of the composite membrane. The carboxylic acids of PAA-AN can dissociate to carboxylate ions at pH 8.5 to provide high charge density in the PAA-AN layer. The volume of the chains is loose and diluted at pH 8.5, but is tight and compact at pH 2.4.

Cu (II) ion exchange

The PAA-AN/filter paper composite membranes can also be used for the removal of metal ions. The adsorption quantity of Cu (II) for the membrane (M-22-400) at different CuSO_4 solution (1, 10, and 100 mmol/L), was studied and the results are presented in Figure 6. The adsorption quantity of Cu (II) from 1 mmol/L solution and 100 mmol/L solution was

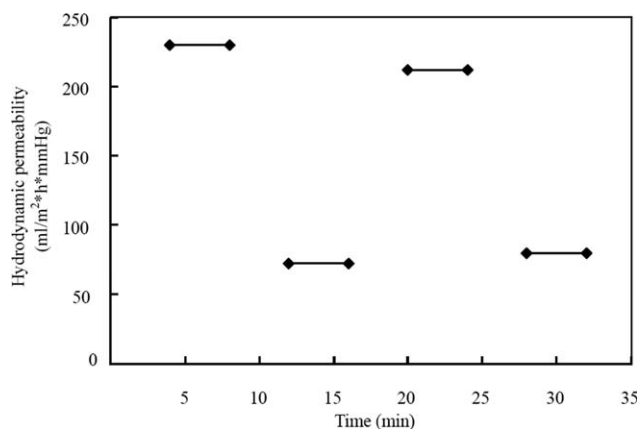


Figure 5 Hydrodynamic permeability for the membrane at 0.5 MPa as the feed was exchanged between pH 2.4 and 8.5 with 4 min equilibration flow followed by 4 min sample collecting (two times collection). Duplicate experiments showed similar results.

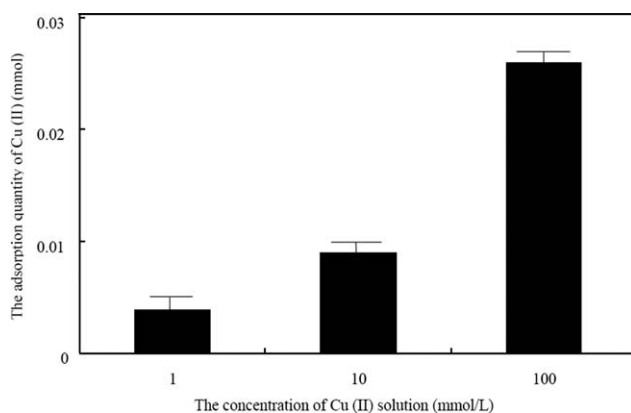


Figure 6 Adsorption quantity of Cu (II) to the membrane (M-22-400) at different CuSO_4 solution. Duplicate experiments showed similar results.

about 0.004 and 0.027 mmol, respectively. The removal ratio of Cu (II) from 1 mmol/L solution and 100 mmol/L solution was about 40 and 2.7%, respectively. It can be seen that the adsorption quantity of Cu(II) increased with the concentration increasing. Besides, the calculated adsorption quantity of Cu(II) for one piece of sample membrane (M-22-400) was about 0.032 mmol. Thus, the Cu(II) amount was excessive in 100 mmol/L CuSO_4 solution for the membrane adsorption, and this led to the lower removal ratio for 100 mmol/L solution. The adsorption quantity of Cu(II) for the membrane (M-22-400) was about 1.18 mmol/g (75.52 mg/g membrane), which was similar to those for the reported membranes,^{16,47} and to the absorption amounts by other reported removal techniques.^{48,49}

Filter paper is made of cellulose and has negligible interactions with Cu (II), whereas the carboxylic groups of PAA-AN have both ion-exchange and complexation abilities. As a counter-ion, Cu (II) could bind to the negatively charged PAA by the electrostatic long-range interactions.^{50,51}

To test the value of retention ratio of Cu (II), 10 mL of 1 mmol/L CuSO_4 solution was applied to the membrane (M-22-400) at pressure 0.05 MPa. The retention ratio of Cu (II) was 38.4% at the experimental condition. These suggested that the prepared composite membranes could accumulate and bind Cu (II) ions, and be used as ion-exchange membranes

CONCLUSIONS

The goal of this study is to develop a new and simple method to prepare pH-sensitive ion-exchange membranes. This had been successfully accomplished by coating PAA-AN copolymer on both sides of filter papers. The water fluxes of these membranes were studied. With the increase of the spin coating speed used to prepare the membranes, the thickness of the membrane decreased; while the

water flux increased. When the thickness of the membranes kept the same, the water flux increased with the increase of the copolymer concentration in casting the solutions due to the increased hydrophilicity. The composite membranes also showed evident pH sensitivity and pH reversibility, and which could be adjusted by the PAA-AN layers. The membranes could bind metal ions, which indicated that the membrane could be used as ion exchange membranes to purify water.

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