

Preparation of a Novel Phthalimidomethylated Polysulfone/Unmodified Polysulfone Blend Affinity Membrane and Applications for Removal of *p*-Nitrophenol

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ABSTRACT: A novel phthalimidomethyl polysulfone (PIPSf)/polysulfone(PSf) blend affinity membrane was prepared and applied for the removal of *p*-nitrophenol from aqueous solutions. In this work, the chloromethylated polysulfone (CMPSf) was used to introduce phthalimido groups onto the polysulfone backbone by Gabriel reaction. The polymers can be easy to phthalimidomethylate to different degrees by control of the reaction temperature and time. Structures of the resulting polymers were confirmed by FT-IR. The obtained polymers showed good solubility in dimethylformamide, dimethylacetamide and formed the affinity membrane blending with polysulfone at different blend compositions by the phase-inversion method. Thus the properties

of films were characterized with respect to water flux, pore size, and porosity. The surface and cross-sectional views of the blend membranes were analyzed by scanning electron microscopy (SEM). The research on treatment of removal *p*-nitrophenol was carried out by affinity membrane process. The adsorption capacity increased with increasing the initial concentration of *p*-nitrophenol in aqueous solution, and the adsorption isotherm fitted the Freundlich model well. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1472–1479, 2011

Key words: chloromethylated polysulfone; chemical modification; blend; affinity membrane; *p*-nitrophenol; adsorption

INTRODUCTION

The nitrophenol compounds are commonly presented in the waste water of chemicals, petrochemicals, and pharmaceuticals industries and are discharged into natural environment. They are also considered as priority pollutants since they have a serious threat to human health and water safety. Meanwhile, nitrophenol compounds possess good chemical, biological stability and difficult to be removed by natural degradation. Therefore, the nitrophenol in the waste water should be treated effectively and reasonably before discharged into the environment. At present the techniques for treating nitrophenol are in the previous study including solvent extraction,¹ adsorption,^{2,3} biodegradation,⁴ photo catalysis oxidation,⁵ and among which, adsorption by polymeric adsorbents has been widely used in recent years. In earlier paper,⁶ a hypercrosslinked polystyrene-type resin HJ-1 was prepared

from chloromethylated poly (styrene-*co*-divinylbenzene) (PS) by Fredel-Crafts alkylation reaction. HJ-1 resin has been used to adsorb *p*-nitrophenol in aqueous solution and shown great efficiency. An amination of polymeric resin adsorbent NA-01 has been prepared by chloromethylated styrene-divinylbenzene copolymer and also obtained great efficiency for treatment *p*-nitrophenol in the literature.⁷ However, these adsorption approaches by polymeric adsorbents are usually subject to certain restrictions, such as low loading capacity or reaction rates, the diffusion restricted and not easy scale-up.

To solve the above problems, one promising and effective mean would be the design of new, high performance affinity membrane chromatography. Affinity membrane has recently proved to be an attractive and competitive method for purifying proteins or other biomolecules from biological fluids. In this work, our new idea was that affinity membrane chromatography could be used to remove *p*-nitrophenol from aqueous solutions. For the first time, we hope to broaden the application field of affinity membrane chromatography. The basic idea here was to replace the polymeric resin adsorbents by affinity membrane. In comparison with resins adsorption, the microporous structure of affinity membranes poses minimal mass-transfer resistance, because they provide large internal surfaces for isolates resulting

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in considerably rapid processing. The membrane chromatography techniques show a higher adsorption and productivity, thanks to its very short-wide bed resulting in a shorter diffusion length and residence times. The affinity membrane chromatography, in particular, offers a number of additional advantages, such as mild operating conditions, no environmental pollution, easier scale-up, reduction of costs and overall consumption of energy.^{8–10}

The physicochemical properties of polysulfone have been proved to be suitable for affinity membrane materials.^{11,12} But, polysulfone materials themselves seem to have a disadvantage that it is less active to offer a large choice of functional groups. Such methods as several papers report the efficiency of amination,¹³ carboxylation,¹⁴ were used to modify polysulfone materials. Among various the membrane material modification processes, chloromethylation modification has already been successfully investigated. The chloromethylated polysulfone, which is very reactive substrates, can further convert model compound with functional groups onto the polysulfone chains in different synthetic ways, under mild conditions. Our lab has successfully reported¹⁵ that the chloromethylation of polysulfone matrix membrane was introduced the mercapto groups for adsorption of Hg²⁺. Lee et al.¹⁶ have firstly synthesized the chloromethylation of polysulfone, and then successfully introduced methylene methacrylate with crosslinkable side-chain in polysulfone. The chloromethylated polymers are easy to attack by nucleophile, further functionalize in aprotic solvents or the presence of phase transfer catalysts.

Amino groups as hydrogen-bonding acceptors are easy to form the hydrogen-bonding with organic compound such as phenol compound as hydrogen-bonding donors. These functional groups have been also introduced onto the matrix of polymeric adsorbents for removal the phenol compound.^{17,18} Consequently, the purpose of this paper is the development of new, inexpensive, high selectivity and chemical, mechanical stable polysulfone affinity membranes with phthalimido groups by chemical modification for removal *p*-nitrophenol in aqueous solution. Our work was relevant to the synthesis of chloromethylated polysulfone, at first. Thus, the chloromethylated polysulfone was transformed into phthalimidomethyl polysulfone (PIPSf) with a imide functional group via nucleophilic substitution reaction. Whereupon, the PIPSf/PSf blend membranes were prepared by phase inversion process. Finally, the obtained membranes with high flux performance were applied to remove the *p*-nitrophenol from aqueous solution. The investigation attempts to detail study of the effect of various parameters such as contact time, and initial *p*-nitrophenol concentration on the adsorption were investigated.

EXPERIMENTAL

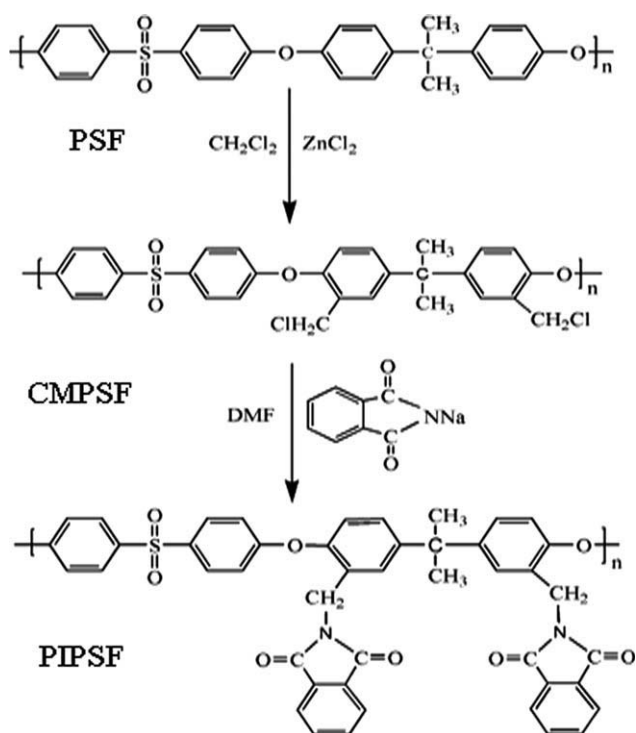
Materials and reagents

The PSf was used as virgin membranes materials and obtained from Tianjin Motimo Membrane Technology (China). Chloromethyl ether was supplied by Nankai University Chemical Plant (China). Phthalimide were procured from Shanghai Chemical Reagent Plant (China). *p*-nitrophenol in analytical grade was purchased from Tianjin Chemical Reagent Plant (China). Sodium hydride (NaH) was purchased from Tianjin Beidouxing Fine Chemical (China). *N,N*-dimethylformamide (DMF), and all other chemicals in analytical grade were used without further purification.

Chemical modification of polysulfone

The CMPSf was performed via the Friedel-Crafts reaction. The PSf was dissolved in dichloromethane, then the mixed solution of chlorodimethyl ether and zinc chloride as the Friedel-Crafts catalyst was added as described in our previous work¹² (see Scheme 1) and the same procedures for CMPSf were employed.

Phthalimidomethylation of CMPSf was described as follows: A solution of refined CMPSf in DMF was added the complex mixture solution of phthalimide, sodium hydride and DMF. The circumfluous reaction lasting about 10 h at 100°C was finished. The



Scheme 1 Process of chemical modification PIPSf from the PSf.

TABLE I
Blend Composition of PSf/PIPSf Affinity Membranes

| Blend composition of polymers 18 wt % | | Additive, PEG 600 wt % | Solvent, DMF wt % |
|---------------------------------------|---------|---------------------------|----------------------|
| PSf % | PIPSf % | | |
| 90 | 10 | 8 | 74 |
| 80 | 20 | 8 | 74 |
| 70 | 30 | 8 | 74 |
| 60 | 40 | 8 | 74 |

solution was cooled to room temperature, then, the solution was slowly added to methanol with vigorous stirring, yielding PIPSf as a lump precipitate, repeatedly washed by distilled water and methanol. The precipitate PIPSf was dried at a temperature 60°C. The nitrogen content of PIPSf was determined via using the Kjeldahl method.¹⁹

IR spectra of PSf and PIPSf

The PSf and PIPSf flat sheet membranes were prepared, and then dried at 50–70°C. The dried membrane plates were placed directly on the ATR crystal and firmly fastened by clips. The infrared spectra of PSf and PIPSf were obtained by Vector 22 Fourier infrared spectrometer.

Preparation of the PIPSf/PSf blend membrane

Preparation conditions of the applied membranes were listed in Table I.

In all the casting solutions, the mass ratio of blending polymers to the total casting solutions was 18 wt %. Casting solutions were prepared as follows: a certain amount of PIPSf and the blend polymer PSf with different mass ratio were dissolved in DMF, using polyethylene glycol (PEG, 600 MW) as the pore former. The homogeneous casting solutions were obtained after stirring for 12 h at room temperature and kept for 24 h in airtight condition to get rid of the air bubbles. Then the casting solutions were poured onto a clear and smooth glass plate with a steel knife to get wet films. After being exposed to air for 30 s, the glass plate along with the polymer film was immersed in the coagulation bath of water at 25°C, then the membranes formed, washed by distilled water, preserved in a 50% glycerin solution for testing.

Observation of PIPSf/PSf blend membrane by SEM

The morphology of the blend membrane samples was observed through JSM-6700F scanning electron microscope. The cross-sectional view of the mem-

branes for the SEM was prepared in liquid nitrogen and breaking it to produce a cross section. All the samples were sputtered-coater with gold.

Characterization of blend membrane structure

Water flux measurements

The experimental equipment was made in Tianjin Polytechnic University, China. The membrane was compacted with distilled water at a higher pressure (0.2 MPa) for about half an hour and until constant water flux was obtained. Finally the water flux was determined at an operating pressure of 0.1 MPa. Measurements were performed in duplicate and averaged. The water flux J was calculated according to the following equation:

$$J = \frac{V}{St} \quad (1)$$

where V is the volume of filtrate (L); S is the effective surface area of the membrane (m^2); t is the sample time (h).

Porosity measurements

The membrane porosity was determined by means of the gravimetry method.²⁰ A prescribed area of wet membrane sample was wiped the glycerol and weighed. Then, the sample was dried in vacuum until a constant mass was obtained. Measurements were carried out in twice and averaged. Percentage porosity of the membrane P_r was calculated from the eq. (2):

$$P_r = \frac{W_1 - W_2}{Sd\rho} \times 100\% \quad (2)$$

where W_1 , W_2 are the mass of the wet and dry sample (g), respectively; d is the average thickness of membrane (cm); S is the area of sample (cm^2); and ρ is the density of glycerol ($g\ cm^{-3}$).

Membrane pore size measurements

The membrane pore size was determined by means of filtering velocity method.²⁰ The membrane pore diameter r_f was obtained:

$$r_f = \sqrt{\frac{8\mu LJ}{Pr\Delta P}} \quad (3)$$

where P_r is the porosity of the membrane (%), L is the thickness of the membrane (m), μ is the viscosity of the transmission liquid ($Pa\ s^{-1}$), J is the flux ($m^3\ m^{-2}\ s^{-1}$), ΔP is the pressure (Pa).

Adsorption experiments of *p*-nitrophenol on affinity membrane

Several 250-mL sealed flasks were introduced into a 100 mL aqueous solution containing different concentration of *p*-nitrophenol (ranging from 10 to 50 mg L⁻¹) respectively, to which the accurately weighted affinity membrane (about 0.10 g) added. The flasks were then shaken under 200 rpm at 298 K for 24 h to ensure adsorption equilibrium. The equilibrium *p*-nitrophenol concentration was determined by UV-spectrophotometer at 317 nm and the equilibrium adsorption capacity of *p*-nitrophenol, Q_e (mg g⁻¹), were calculated according to eq. (4):

$$Q_e = \frac{V(C_o - C_e)}{m} \quad (4)$$

where V is the volume of solution (L); m is the weight of dry affinity membrane (g); C_o and C_e is the initial and balanceable concentration of *p*-nitrophenol in aqueous solution (mg L⁻¹), respectively.

RESULTS AND DISCUSSION

Optimal reaction conditions of chemical modification polysulfone

The functionalized polysulfone (PIPSf) was carried out by two steps, which are chloromethylation followed by phthalimidomethylation as shown in Scheme 1.

The CMPSf was first performed according to our previous study.¹² The chlorine content of CMPSf was determined to be 7.57% by using the Woolhad method. Then, under the mild condition, CMPSf and sodium salt of phthalimide could take place nucleophilic substitution reaction, in which, phthalimide anion was selected as a nucleophile. Sodium salt of phthalimide was prepared by the reaction of phthalimide and NaH in dimethylformamide solution. In the nucleophilic substitution reaction process, phthalimide anion firstly attacked the center carbon atom of the chloromethyl. At the same time, chlorine atoms were off. At this time, C—N bond was formed; C—Cl bond was ruptured. Then, the strengthening of the nucleophile with the central carbon atom was gradual aggrandized, the promising product (PIPSf) was obtained.

TABLE II
Result of PIPSF Synthesized in Different Solvent

| Solvent | Dipole moment μ (D) | Dielectric constant ϵ (F m ⁻¹) | Results |
|------------|-------------------------|---|--------------------|
| Dioxane | 0.45 | 2.2 | No reaction |
| Chloroform | 1.08 | 5.2 | Almost no reaction |
| DMF | 3.82 | 37.0 | Complete reaction |

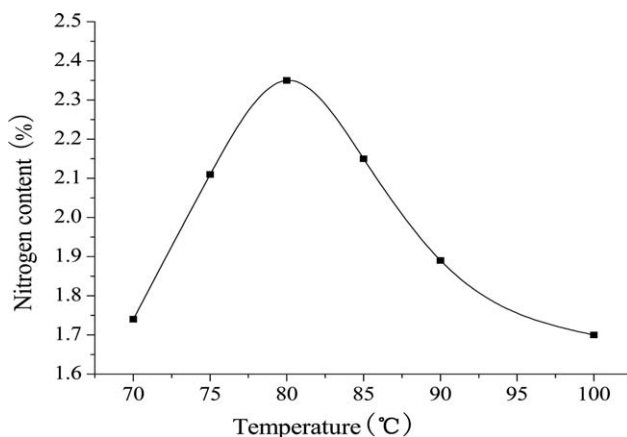


Figure 1 Influence of reaction temperature on PIPSf nitrogen content CMPSF: 10 g; NaH: 1.2000 g; Reaction time: 12 h.

To optimize the reaction conditions, a variety of factors, such as reaction solvent, reaction temperature and reaction time impacting on the nucleophilic substitution reaction were evaluated.

Effects of reaction solvent

In nucleophilic substitution reaction, sodium salt of phthalimide as a nucleophile should be appeared in the form of free ionic and formed transition state with reactant mixture. Therefore, the solubility of CMPSf was the key of reaction process. So the contrast experiments to different solvent systems were carried on respectively, in Table II.

The results showed that the desired product was not able to obtain, when chloroform and dioxane were used as solvent. However, in the nonprotonation solvent DMF, the CMPSf was dissolved sufficiently; negative ion of phthalimide was the very strong nucleophile, the nucleophilic reaction can be carried out smoothly. Finally the obtained product was PIPSf after analysis.

Influence of temperature on PIPSf nitrogen content

Nitrogen content measurements were plotted with respect to temperature in Figure 1.

It can be seen from the Figure 1 that increases of nitrogen content were connected with increases in temperature. When the temperature was controlled at 80°C, its nitrogen content was the highest. In the nucleophilic substitution reaction, along with temperature increasing, steric hindrance of sodium phthalimide decreased, its nucleophilic ability enhanced, and the activation energy was the highest. Therefore, as the reaction temperature increasing, the reaction rate accelerated significantly. However, with the reaction temperature continues to rise, nitrogen content would be dropped, probably crosslinking reaction or side

TABLE III
Influence of Reaction Time on PIPSF Nitrogen Content

| Reaction time (h) | 8 | 10 | 12 |
|----------------------|------|------|------|
| Nitrogen content (%) | 1.93 | 2.31 | 2.34 |

effects may occur because the temperature was too high, resulting in a low productivity.

Influence of reaction time on PIPSF nitrogen content

Data of nitrogen content with respect to treatment time was shown in Table III.

From the results, as can be seen that nitrogen content increased as the reaction time. At the initial reaction stage, the reaction rate was fast, nitrogen content rapidly increased. 10 h later, the nitrogen content increased slowly, so further extending the reaction time was largely meaningless. We presumed on the basis of reaction mechanism that the phthalimido groups were once fixed on the chloromethyl, depleted the attractive reactivity position, and reduced the rate of subsequent nucleophilic substitutions.

IR characterization of polymers

In this experiment, the IR analysis was used for the characterization of the synthetic polymer structure and the identification of functional groups existing. The infrared spectra of samples were shown in Figure 2

As shown in infrared spectra of PSf, the characteristic absorption peak of $-\text{SO}_2$ bond vibration was determined at 1102.98 cm^{-1} . The C—H bond vibration of the main chain $-\text{CH}_3$ had a characteristic absorption peak at 2966.82 cm^{-1} . The band at 1241.14 cm^{-1} was C—O vibration of aromatic ether. In the infrared spectra of CMPSf, the absorption peak of the PSf still existed, but a new peak for C—Cl was appeared in 660.71 cm^{-1} . After phthalimidomethylation of CMPSf, the absorption peak of C—Cl was almost disappeared, a new peak for the carbonyl groups (C=O) was appeared in 1772.34 and 1715.70 cm^{-1} , respectively. At the same time the absorption peaks at 1391.10 cm^{-1} was C—N bond stretching vibration of phthalimido groups. The changes in the above-mentioned peaks were fully showed that CMPSf with sodium phthalimide have taken place the nucleophilic substitution reaction and generated the desired product, namely was PIPSF. The around 3400 cm^{-1} was the characteristic absorption peak of hydroxyl, because the water was in the samples of IR analysis.

Structural properties of blend affinity membrane

The chemical modification procedure shows key advantages: simplicity, low cost, and easy to controlled conditions. The chemical modification of polymers can

resist membrane fouling, but also obtain the perfect adsorption performance. But, functionalization of polymers resulted in polymers degradation and a decline of physical and chemical properties. So, to improve the membrane mechanical properties, the obtained phthalimidomethylated polysulfone would blend with unmodified polyulfone and the blend membranes were prepared by phase inversion process. Film-forming phase inversion process is nonequilibrium process, thereby blend mass composition of polymer have a particularly important impact on the membrane performance (water flux, pore size, and porosity). The effect of different PIPSF/PSf blend composition on water flux, pore diameter, porosity was investigated. The results were showed in Table IV.

From the results, it can be showed that the membranes based on PIPSF and PSf were prepared and the maximum possible blend composition was found to be 40/60% of PIPSF/PSf, the PIPSF content was further increased, the phase separation would take place during membrane formation. The reason was seemed to attribute to the strong affinity interactions within the PIPSF phase. In case of PIPSF/PSf blend membranes, as the PIPSF content increases from 10 to 40%, the steady state flux also increases from 80.34 to $138.76\text{ (L m}^{-2}\text{ h}^{-1}\text{)}$, the porosity and pore diameter of the membranes also increased. PIPSF was a charged polymer; the electrostatic repulsion between PIPSFf molecules would lead to larger pore size or interconnected pores owing to increased segmental gap between the polymeric chains.²¹ Therefore, water flux, pore diameter and porosity of the resultant membranes were all increased. For further separation studies, PIPSF/PSf blend membranes with 20/80 and 40/60% composition were selected and the results are discussed.

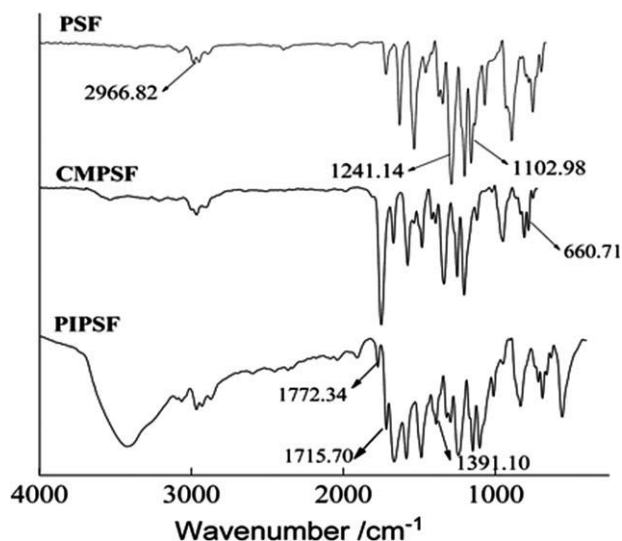


Figure 2 The IR spectrum of polymers (PSf, CMPSf, and PIPSF).

TABLE IV
Effect of Different Blending Ratio on PIPSf/PSf Membrane Structure

| Blend composition of polymers | | Water flux ($\text{L m}^{-2} \text{h}^{-1}$) | Pore diameter (nm) | Porosity (%) |
|-------------------------------|--------------|--|--------------------|--------------|
| PIPSf % (wt %) | PSf % (wt %) | | | |
| 10 | 90 | 80.43 | 23.16 | 56.73 |
| 20 | 80 | 96.65 | 26.13 | 60.47 |
| 30 | 70 | 120.34 | 32.97 | 74.12 |
| 40 | 60 | 138.76 | 35.83 | 80.32 |

Morphology of blend membrane characterized by SEM

The SEM has been proved an important tool for the determination of the morphology of the membranes. The surface and cross-sectional view of the PIPSf/

PSf blend membranes (20/80 and 40/60%) were showed in Figure 3.

From the surface figures sectional view of the PIPSf/PSf blend membranes it can be seen that the distribution of membrane pore was more uniform. A

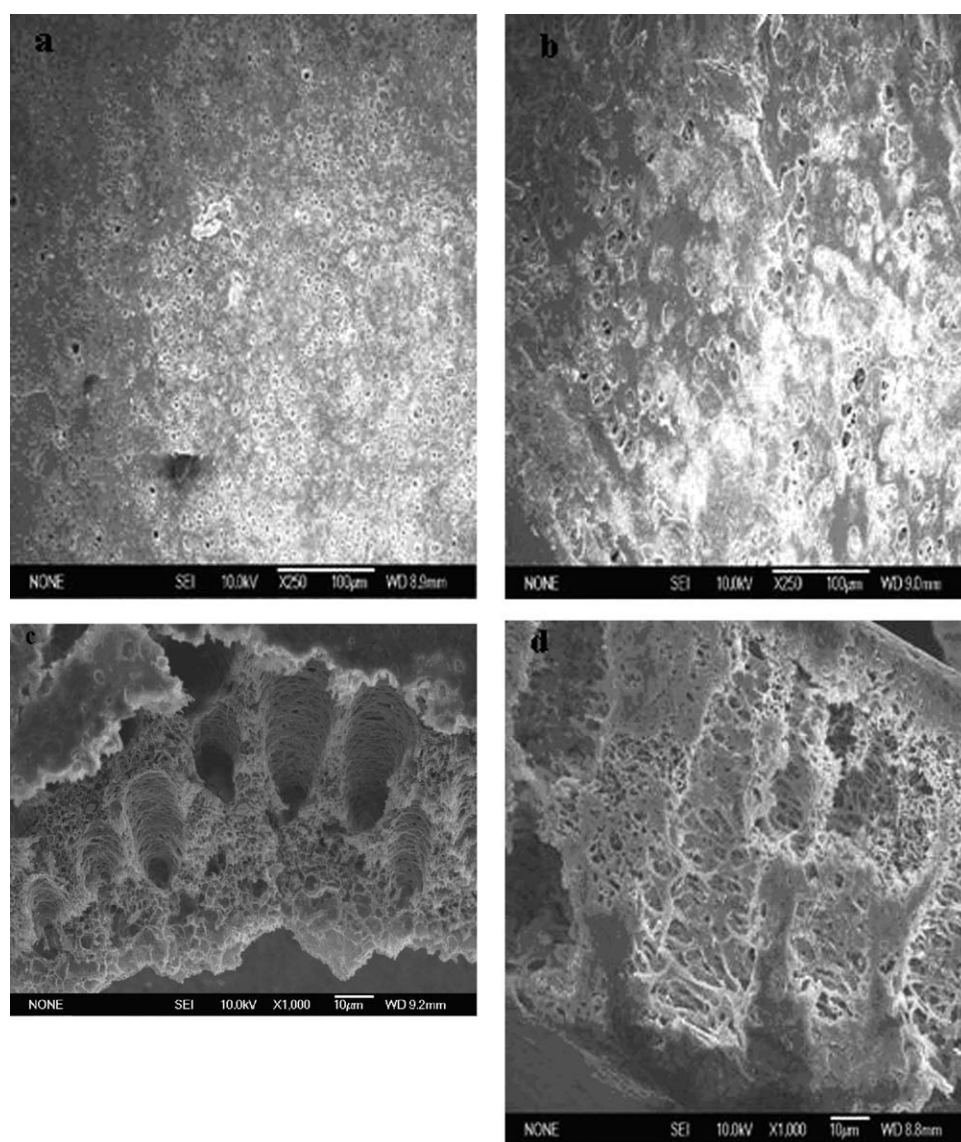


Figure 3 The surface and cross section morphology of blending membrane. a: The surface section morphology of PIPSf/PSf (20/80%) blending membrane; b: The surface section morphology of PIPSf/PSf (40/60%) blending membrane; c: The cross section morphology of PIPSf/PSf (20/80%) blending membrane; d: The cross section morphology of PIPSf/PSf (40/60%) blending membrane.

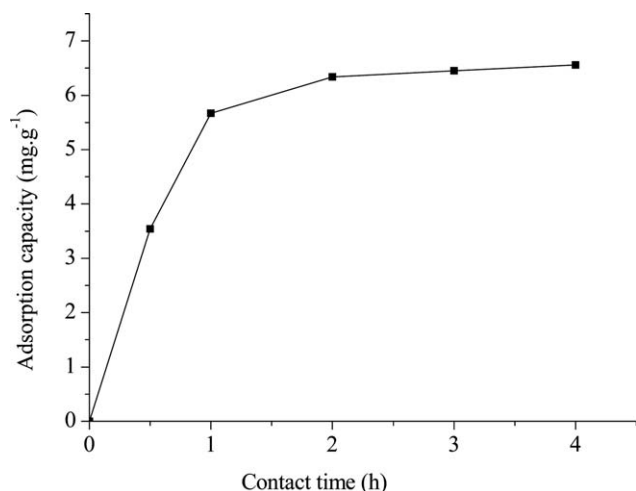


Figure 4 Effect of contact time on *p*-nitrophenol adsorption capacity. Initial solution concentration: 30 mg L⁻¹; at 25°C.

large pore, relatively thick skin layer and finely porous substructure was showed throughout the cross section morphology of the membrane. In the case of 20/80% PIPSt/PSf blend membrane, the number of large pore was less compared to 40/60% PIPSt/PSf membranes. These results supported that water flux, pore diameter and porosity of the PIPSt/PSf blend membranes enhanced with the PIPSt content.

Adsorption studies

Effect of contact time on the sorption amount of the membrane for *p*-nitrophenol

In this experiment, the effect of contact time on adsorption of *p*-nitrophenol compounds by affinity membrane was showed in Figure 4.

It can be seen that the adsorption equilibrium of *p*-nitrophenol was achieved after one hour. Almost, no remarkable improvement was observed after longer contact time. Initially, the concentration of *p*-nitrophenol in the solution was relatively high, a large number of active groups on the affinity membrane were available for adsorption, so the adsorption rate was very fast, thus adsorption capacity of *p*-nitrophenol increased rapidly within the one hour of adsorption. With the adsorption reaction performed, the rate of adsorption decreased significantly because of diffusion-limited. Meanwhile, it was also showed that affinity adsorption was chemical adsorption, and it was difficult to achieve equilibrium.

Effect of the initial solution concentration on the sorption amount of the membrane for *p*-nitrophenol

The adsorption of *p*-nitrophenol by the affinity membranes was studied at different initial *p*-nitrophenol

solution concentrations (ranging from 10 to 50 mg L⁻¹). As it can be seen in Figure 5.

The adsorption capacity of *p*-nitrophenol on the membrane increased from 3.85 to 11.23 mg g⁻¹, as the concentration of *p*-nitrophenol. The results showed that the higher initial solution concentration formed a higher concentration gradient between aqueous and solid phases, provided a higher mass transfer resistance and accelerated the probable collision between *p*-nitrophenol and affinity membranes.

Adsorption isotherms of *p*-nitrophenol on the affinity membrane

The adsorption of *p*-nitrophenol onto the affinity membrane was determined in the *p*-nitrophenol concentrations ranging from 10 to 50 mg L⁻¹. The adsorption data can then be correlated with the Freundlich isotherm models equations. The Freundlich equation is the empirical relationship whereby it is assumed that the adsorption energy of *p*-nitrophenol binding to a site on an adsorbent depends on whether or not the adjacent sites are already occupied. The Freundlich isotherm model is usually adopted for heterogeneous adsorption. This isotherm can be described as follows:

$$Q_e = K_F(C_e)^{1/n} \quad (5)$$

The isotherm can be transformed to a linear form as follows:

$$\lg Q_e = \lg K_F + \frac{1}{n} \lg C_e \quad (6)$$

where Q_e is the adsorption capacity at equilibrium (mg g⁻¹), C_e is the equilibrium concentration of

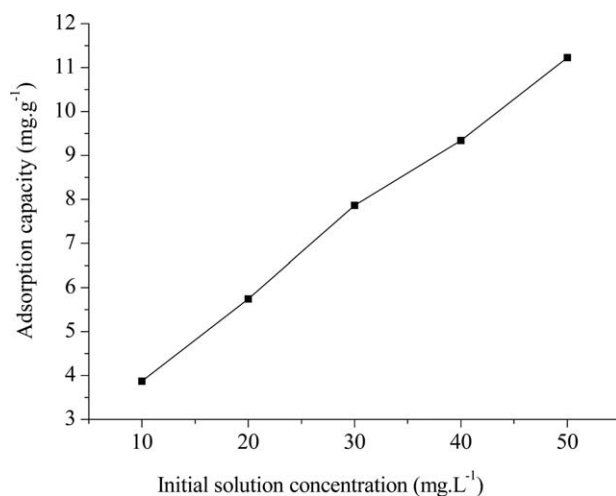


Figure 5 The relation of adsorption capacity and the initial solution concentration of *p*-nitrophenol Contact time: 16 h; at 25°C.

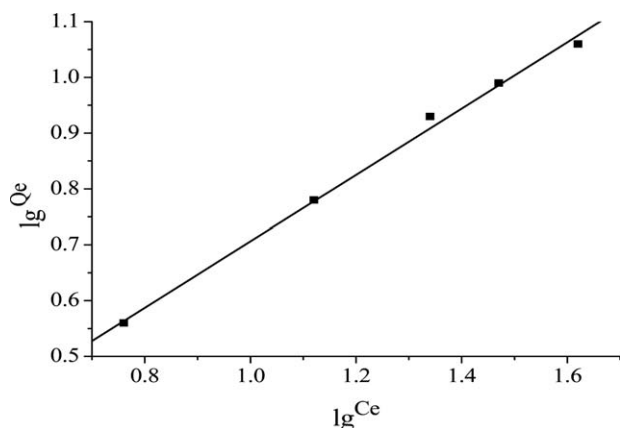


Figure 6 Freundlich plot of *p*-nitrophenol on the affinity membrane. The data are from the above isothermal adsorption experiment.

p-nitrophenol in solution, K_F and n are the physical constant of the Freundlich adsorption isotherm. The K_F and n are the indicators of the adsorption capacity and adsorption intensity, respectively. Figure 6 showed that the logarithm of adsorption capacity Q_e and the *p*-nitrophenol equilibrium concentration C_e .

The correlation coefficient of the Freundlich isotherm (R^2) was 0.9976. The slope of the linear was equal to $1/n$ and the constant n was 1.68, it was indicated that the adsorption process was easy to carry out. Therefore, a better-fitted straight line with high correlation coefficient was obtained in case of the Freundlich model. This suggested that the adsorption data was well represented by Freundlich isotherm model and support the assumption that adsorption took place on heterogeneous surfaces.

CONCLUSIONS

The novel polysulfone membrane material (PIPSf) with methylated phthalimido groups was successfully synthesized by the Friedel-Crafts and Gabriel reaction. The nitrogen content of the PIPSf can be readily controlled by adjusting the reaction temperature and time. The optimal reaction temperature and time were at 80°C and 10 h, respectively. These PIPSf with good thermal and oxidative stability can form tough and flexible membranes blending with

polysulfone via phase inversion. When the blend composition of PIPSf/PSf was 40/60%, the prepared affinity membrane showed high water flux. The membrane can adsorb more efficiently *p*-nitrophenol in aqueous solution. The equilibrium adsorption capacities of *p*-nitrophenol increased with the initial *p*-nitrophenol solution concentration. The Freundlich isotherm models gave a good fitting for all the adsorption isotherms.

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